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SYNTHESIS AND CHARACTERIZATION OF BIS(CYCLOPENTADIENYL)URANIUM(IV) COMPLEXES

by

© ANITA L. ARDUINI

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SYNTHESIS AND CHARACTERIZATION OF BIS(CYCLOPENTADIENYL)URANIUM(IV) COMPLEXES submitted by Anita L. Arduini in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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Date August 11, 1978

TO MY FAMILY

Abstract

The reagent, $Cp_2U(NEt_2)_2$, was formed from a reaction of $U(NEt_2)_4$ with cyclopentadiene. The reactive nature of the uranium-nitrogen bonds in the starting tetrakis-amide complex was retained by $Cp_2U(NEt_2)_2$. This compound underwent both acid displacement and insertion type reactions to yield a variety of pseudo-six-coordinate complexes of the formula, $Cp_2U(chelate)_2$ where chelate = O_2CNEt_2, $OSCNEt_2$, S_2CNEt_2, O_2CPh, O_2CMe, O_2CCMe_3, OSCPh, OSCMe, cis-(OCMe)$(OCCHMe_2)Re(CO)_4$, cis-$(OCMe)_2Re(CO)_4$. The compounds, $Cp_2U(OSCNEt_2)_2$, $Cp_2U(S_2CNEt_2)_2$, and $Cp_2U(OSCPh)_2$ were monomeric, $Cp_2U(O_2CCMe_3)_2$, dimeric and $Cp_2U(O_2CNEt_2)_2$, polymeric in solution, as determined from molecular weight measurements. The spectroscopic data of the compounds are consistent with the designated chelate coordination of the ligands and a pentahapto bonding mode for the cyclopentadienyl rings. The complexes are considered to have octahedral geometry with the ligands and Cp rings in mutually cis positions. The variable temperature ^1H NMR data of $Cp_2U(OSCNEt_2)_2$, $Cp_2U(S_2CNEt_2)_2$, $Cp_2U(OSCPh)_2$, and $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ indicated that metal-centered rearrangement processes were averaging non-equivalent environments of the chelate ligands. The carbamates were also assumed to have restricted rotation about the carbon-nitrogen bonds. The $\Delta G^{\ddagger}$ value for the rearrangement in

$Cp_2U[cis-(OCMe)_2Re(CO)_4]_2$ was calculated to be 13.5 ± .5 kcal/mole in toluene and 13.7 ± .4 kcal/mole in CH_2Cl_2 at a coalescence temperature of 35°C. The rearrangements in the other complexes were still proceeding rapidly even at the lowest accessible temperatures. The dimeric structure of $Cp_2U(O_2CCMe_3)_2$ was assumed to contain four symmetrically bridging carboxylate ligands as the ^1H NMR data only showed one methyl resonance.

The reagent, $Cp_2U(NEt_2)_2$, underwent aminolysis reactions with $HNPh_2$, HNC_4H_4, $HNC_4H_2Me_2$ and $HNC_4Me_3(COOEt)$. The compounds, $Cp_2U(NEt_2)(NPh_2)$ and $Cp_2U[NC_4Me_3(COOEt)]_2$ were isolated in a pure form whereas the other pyrroles gave mixtures of mono- and bis-substituted complexes.

Attempts to make dichloro containing compounds of the type $Cl_2U(NR_2)_2$ from UCl_4 and the lithio or potassio salts of amines were not completely successful. Although pure $Cl_2U[N(C_6H_{11})_2]_2$ was obtained, the other complexes, $Cl_2U[N(SiMe_3)_2]_2$ and $Cl_2U(NEt_2)_2$, were contaminated with the trisamide compounds, $ClU(NR_2)_3$. Subsequent reactions with cyclopentadiene did not produce pure Cp_2UCl_2 but mixtures of Cp_2UCl_2 and Cp_3UCl.

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ABBREVIATIONS

COT - cyclooctatetraenyl, C_8H_8

Cp - η^5-cyclopentadienyl, C_5H_5

Ind - η^5-indenyl, C_9H_9

Me - methyl, CH_3

Et - ethyl, C_2H_5

Ph - phenyl, C_6H_5

Py - pyridine

iPr - iso-propyl, $CH(CH_3)_2$

acac - acetylacetonato

β-diketonate - β-ketoenolate ion, $RC(O)CHC(O)R^-$.

THF - tetrahydrofuran

dme - 1,2-dimethoxyethane

CHAPTER ONE

GENERAL INTRODUCTION TO BIS(CYCLOPENTADIENYL)URANIUM(IV) CHEMISTRY

Actinide organometallic chemistry dates back to the early 1940s with the Manhattan project in the United States, however interest in the field has been quite minimal up until approximately 1968 when the reported synthesis of the complex "uranocene", $U(COT)_2$,[1] stimulated research in organoactinide chemistry. Before 1968, the work done, while not expansive, was certainly important in that it laid the foundation for a large amount of work that came later and still continues.

The major area of study has been concerned with derivatives of tris(cyclopentadienyl)uranium(IV) and thorium(IV). Wilkinson and Reynolds[2] initiated work on Cp_3UR compounds with their report in 1956 on the synthesis of Cp_3UCl and preliminary characterization of Cp_4Th. Later E. O. Fischer's group reported their synthesis of Cp_4U [3] and an improved synthesis and characterization of Cp_4Th.[4] These compounds were studied by at least two groups interested in interpreting the NMR spectra of paramagnetic molecules with respect to contact and pseudo-contact mechanisms.[5,6,7] A paper by Anderson and Crisler in 1969 characterized more fully Cp_4U, Cp_3UCl and Cp_3UBH_4 by infrared, electronic and mass spectroscopy.[8]

At the start of the thesis work in 1973, there were still only two main areas of organouranium chemistry, derivatives of both tris(cyclopentadienyl)uranium(IV) and uranocene. Streitwieser *et al.* reported the full preparation and properties of uranocene[9] and shortly afterwards alkyl and aryl derivatives derived from Cp_3UCl [10,11] and studies on selected alkoxy derivatives of $Cp_3U(IV)$ were published.[12] The early work in organoactinide chemistry as well as reviews of the literature up to 1976 have been published.[13] A short summary of work done in this field since that time follows.

It is apparent that organoactinide chemistry is expanding through the use of more novel ligand systems. Streitwieser has prepared a number of substituted uranocenes containing alkyl, alkoxy and amino groups.[14] One of these compounds, 1,1'-di-n-butyluranocene, has been investigated as a reagent for the reduction of nitro compounds and related derivatives.[15] A uranium metallocarborane complex $[U(C_2B_9H_{11})_2Cl_2]^{2-}$ was isolated by Raymond *et al.*,[16] in which the dicarbollide dianion exhibits bonding properties intermediate between cyclooctatetraene dianion and cyclopentadienide moieties. An interesting reaction between Cp_3UR and AlR'_3 was described by Vasil'ev *et al.*[17] This interaction produced new Cp_3UR' compounds through a postulated exchange of alkyl radicals. Extending the indenyl chemistry of the actinide elements, Goffart *et al.* published two papers describing the preparation of $(Ind)_3MR$ [M = Th or U, R = Me or $n\text{-}C_4H_9$][18] and $(Ind)_3MI$ [M = Th or U].[19] A recent publication[20] on the reactivity of mono(Cp) uranium-(IV) complexes describes, among others, species of the type $[CpUX_3L_2]$ X = Cl, Br; L = $Me_3CCONMe_2$, PPh_3O; $CpUCl_3L_2$ L = $MeCONMe_2$ and $[CpUX_3L]_2$ X = Cl, Br; L = $Ph_2(O)PCH_2CH_2P(O)Ph_2$. Spectroscopic and molecular weight determinations indicate that many of the compounds exhibit associated behavior.

Compounds have been reported which do not contain multihapto ring bonding but do have uranium to carbon sigma bonds. Two examples are the lithium alkyl anions of uranium(IV) $Li_2UR_6 \cdot 8Et_2O$ (R = Me, CH_2SiMe_3, Ph and $o\text{-}Me_2NCH_2C_6H_4$)[21] and the complex, $(C_6H_5CH_2)_4U \cdot MgCl_2$.[22]

The preceding brief summary of organouranium chemistry illustrates that one area that has been almost completely neglected has been the study of derivatives of bis(cyclopentadienyl)uranium(IV). This situation is a result of a lack of an appropriate precursor for the preparation of compounds containing the Cp_2U moiety. The logical choice, Cp_2UCl_2, has actually been reported in the chemical literature.[23] However, it was later shown that the compound obtained in this reaction is best represented as $(Cp_3U)_2UCl_6$ [24] and that Cp_2UCl_2, if formed at all during the synthesis, is unstable toward disproportionation to give the Cp_3U^+ complex. Indications of another approach to Cp_2U type chemistry were provided by examples of work done with the early transition metals. Lappert ~~*et al.*~~[25] had demonstrated the synthetic utility of transition metal amides through the reactivity of the M-N bonds towards molecules that contained either dipolar multiple bonds or acidic hydrogens. The reactions of the tetrakis(amides) of Zr and Hf with cyclopentadiene proceeded very cleanly to give the bis(cyclopentadienyl) substituted products. The starting point for our research then became the synthesis of tetrakis(amide) derivatives of uranium(IV), in the hope that Cp_2U derivatives would be forthcoming.

As early as 1956 Gilman *et al.* [26] prepared uranium (IV) amides, alkoxides and mercaptides, however the further synthetic utility of these compounds was not investigated. The reactivity of the few thorium compounds that had been prepared was not studied further either.[27,28] The reactivity of one of Gilman's compounds, $U(NEt_2)_4$, towards the weakly acidic species cyclopentadiene was investigated by this research group.[29] The compound, $Cp_2U(NEt_2)_2$, was produced fairly easily and showed promise as a useful starting reagent for Cp_2U chemistry, since it reacted quite rapidly with CS_2 to form the insertion product $Cp_2U(S_2CNEt_2)_2$,[29] hence demonstrating the reactivity of the uranium-nitrogen bonds.

The systematic study of the reactivity of $Cp_2U(NEt_2)_2$ was then pursued in the expectation that new Cp_2U derivatives could be prepared and their properties investigated.

During the time the thesis work was in progress a number of Cp_2U type compounds have been reported. They consist of the ring-bridged halides $[X(C_5H_4)_2]_2U_2Cl_5^-Li^+-(THF)_2$, where X = CH_2, Me_2Si and $CH_2CH_2CH_2$,[30] some bis-(pentamethylcyclopentadienyl) derivatives, $(Me_5C_5)_2UR_2$ where $R_2 = Cl_2$, Me_2, C_4Ph_4, $(Me_5C_5)_2U(Cl)Me$, and $[(Me_5C_5)_2UH_2]_2$ synthesized by Marks,[31] a tetrahydroborate complex $Cp_2U(BH_4)_2$[32] and an interesting bridge-dimer compound synthesized by Cramer, $[\mu-(CH)(CH_2)P(C_6H_5)_2UCp_2]_2$.[33] Other uranium(IV) compounds containing two pentahapto ligands are the indenyl complexes $(Ind)_2UMe_2$, $(Ind)_2U(C_4H_9)_2$[34] and the dicarbollide containing compound, $[U(C_2B_9H_{11})_2Cl_2]^{2-}$.[16]

It has been common among researchers in this field to make chemical comparisons between organoactinide complexes and transition metal organometallic compounds. Correlations are drawn with the d-orbital metals rather than with the ionic organolanthanide compounds because the organouranium species tend to possess bonding that can be considered more covalent than ionic.[35] The increased covalency of uranium bonds has been ascribed to the participation of f-orbitals of suitable symmetry and energy on the uranium centre with ligand orbitals. A number of photoelectron spectroscopic studies[36,37,38] have concluded that there is demonstrated f-orbital covalency for Th and $U(COT)_2$ compounds and it is suggested that this interaction may be present in other organoactinide species as well.

There are differences between organouranium and, specifically, early transition metal chemistry which can be related to the larger ionic radius of uranium in the +4 oxidation state and the tendency of uranium towards higher coordination numbers. As well there are similarities with respect to chemical reactivity, structural configurations and stereochemical behavior.

This work is a further attempt to increase the knowledge of both organouranium chemistry and those physical and chemical phenomena which are also observed in transition metal chemistry.

CHAPTER TWO

AMIDE DERIVATIVES OF BIS(CYCLOPENTADIENYL)URANIUM(IV)

Introduction

The impetus to develop amido derivatives of $Cp_2U(IV)$ resulted from the inability to prepare Cp_2UCl_2. This compound could have been the starting material for a wide range of Cp_2U containing compounds, as is the case with Cp_2MCl_2 in transition metal chemistry. A number of reasons can be postulated for the difficulty in obtaining pure Cp_2UCl_2. This compound is nominally eight coordinate (assuming that the Cp group occupies three coordination positions), which is a relatively low coordination number for uranium. The presence of the ten-coordinate species, Cp_3UCl, in all preparations of Cp_2UCl_2 possibly reflects the greater stability of the higher coordination number environment. The Cp_2UCl_2 system was studied quite extensively by Jamerson as part of his thesis work.[39] The system was quite complicated and was not completely resolved, however it was apparent that disproportionation reactions were taking place involving Cp_2UCl_2, $CpUCl_3$, UCl_4 and $(Cp_3U)_2$-UCl_6. Spectral analysis of the mixtures was also hindered by the unfortunate chemical shift similarity of the Cp protons of $CpUCl_3$, $(Cp_3U)_2UCl_6$ and Cp_2UCl_2 in the ^1H NMR spectra.

This apparent lability of the Cp moiety in an organometallic system has been observed for the cyclopentadienyl tin(IV) halide system. Two groups studied this system and found that disproportionation and redistribution reactions were quite common among the Cp_nSnHal_{4-n} (Hal = Cl, Br, I) compounds.[40,41] For both the tin and uranium cases, the choice of solvent can be significant. The donor solvent, THF, in both systems increases the rate of the reactions. As well in many systems where group transfer reactions are observed, the Cp moiety is one of those groups. This is not surprising since the Cp ligand is very flexible with respect to changes in its coordination mode from monohapto to pentahapto and vice versa. There are examples of compounds containing both η^1- and η^5-cyclopentadienyl groups such as Cp_4Ti,[42,43] and Cp_4Hf,[44] where X-ray analyses indicated that they possessed two pentahapto and two monohapto ligands. As well the ^1H NMR spectra of these compounds indicate that rapid intramolecular exchange of the groups is occurring. The coordination of bridging five-membered rings, such as is found in the compound $[Th(C_5H_5)_2-(C_5H_4)]_2$,[45] can also be envisaged as a transition-state for a cyclopentadienyl transfer in the tin and uranium systems. For this compound each thorium atom is η^5-bonded to three Cp groups and η^1-bonded to one of the Cp rings of the other thorium.

The evidence to date suggests that the tenuous existence of Cp_2UCl_2 may be due to either the availability of coordination sites resulting from the low steric requirement of the Cp group or the previously mentioned flexibility of the Cp ligand.

Other research groups have approached the problem of stabilizing the Cp_2U type system by a number of different ways. One solution is to link the two Cp rings together. This approach was pursued by Marks using a ligand $[X(C_5H_4)_2]^{2-}$ where X = CH_2, Me_2Si and $CH_2CH_2CH_2$. However, instead of the expected compounds of the type, $X(C_5H_4)_2UCl_2$, the ten coordinate dimeric complexes $[X(C_5H_4)_2]_2U_2Cl_5^-Li^+(THF)_2$ were formed,[30] again illustrating the tendency towards higher coordination. These compounds react with the Lewis bases, 2,2'-bipyridyl and 1,10-phenanthroline to form the adducts $X(C_5H_4)_2UCl_2 \cdot B$. It would seem that joining the Cp group together stops ring transfer but does not hinder the attainment of ten coordination.

The eight-coordinate compounds $(Ind)_2UMe_2$ and $(Ind)_2U(C_4H_9)_2$ were isolated from an *in situ* preparation of $(Ind)_2UCl_2$.[34] The presence of the bulky indenyl ligand effectively blocks coordination sites and in so doing stabilizes the eight-coordinate complex. The use of a sterically demanding group was also the approach taken by Raymond *et al.* for the synthesis of the anion $[(C_2B_9H_{11})_2UCl_2]^{2-}$.[16] The dicarbollide ligand could also hinder disproportionation reactions because initial association of the charged species and formation of the -3 charged anion $[(C_2B_9H_{11})_3UCl]^{3-}$ would not be favoured. The reaction of this anion with $C_8H_8{}^{2-}$ and $C_5H_5{}^{-}$ produced uranocene and mixed ligand complexes of cyclopentadienyl and dicarbollide dianions respectively.

Certainly one of the more promising compounds synthesized to date is the complex $(Me_5C_5)_2UCl_2$.[31] In solution the compound has been shown to be monomeric which suggests again that a large group, in this case the pentamethylcyclopentadienyl ring, prevents association and group transfer. The chlorine atoms in this compound are still reactive and are easily replaced with alkyl groups by using lithio reagents.

Another way of stabilizing the Cp_2U fragment would be to employ ligands containing lone pairs of electrons which could donate electron density to the metal centre through a π type interaction. A precedent for this situation has been known for the transition metal amides. The chemistry of these compounds is quite varied owing to the stabilization of unusual coordination numbers and the reactivity of the metal-nitrogen bonds.[46,47] Of special interest was the reaction of acidic hydrocarbons, in particular the reagent cyclopentadiene, with the transition metal amides. The Cp_2M containing amides were obtained for the early transition metals as shown below.[25]

$$M(NMe_2)_4 + \text{excess } CpH \longrightarrow Cp_2M(NMe_2)_2 + 2HNMe_2 \qquad (II\text{-}1)$$

$M = Zr, Hf$

The remaining metal-nitrogen bonds were quite labile undergoing acid displacement reactions.[48]

$$Cp_2M(NMe_2)_2 + 2RH \longrightarrow Cp_2M(R)_2 + 2HNMe_2 \qquad (II\text{-}2)$$

$RH = ROH, RSH, RNH, PhC{\equiv}CH$

Based on the obvious success of the transition metal dialkyl amides as versatile reagents towards the formation of organometallic compounds, a similar reaction procedure was considered for uranium and thorium.

Reactivity of Actinide Tetrakisamides

The initial work on tetrakisamides of thorium and uranium in this research group was done by J. D. Jamerson. The very air and moisture sensitive compounds $M(NR_2)_4$, M = Th and U, R = Me, Et, iPr and Ph were synthesized according to the following reaction.

$$MCl_4 + 4LiNR_2 \longrightarrow M(NR_2)_4 + 4LiCl \qquad (II\text{-}3)$$

Spectral studies indicated that monomeric, four-coordinate species were obtained for all but the dimethyl- and the diethylamido compounds. These results have been partially confirmed by structural work done by Edelstein *et al.* on a series of uranium tetrakisamides. They determined that $U(NEt_2)_4$ is a five-coordinate dimeric complex[49] and that $U(NPh_2)_4$ is a four-coordinate monomer.[50] Using the dilithio salt of N,N'-dimethylethylenediamine, they isolated two complexes, the trimeric compound $U_3(MeNCH_2CH_2NMe)_6$ [51] and the tetrameric compound $U_4(MeNCH_2CH_2NMe)_8$.[52] The association of the uranium amides is in contrast to the behaviour found for transition metal species. The compound $Mo(NMe_2)_4$ has been shown to have a tetrahedral monomeric structure in the solid state.[53]

The next step in the project was to examine the reactivity of the tetrakisamides towards the weak acid cyclopentadiene. It was found that $U(NEt_2)_4$ and $U(NPh_2)_4$ formed the corresponding pure $Cp_2U(NR_2)_2$ compounds when reacted with two equivalents of cyclopentadiene. Neither $Th[N(iPr)_2]_4$ or $U[N(iPr)_2]_4$ would react with cyclopentadiene, probably due to the very bulky isopropyl group which is effectively blocking the approach of the cyclopentadiene moiety. The reaction of $U(NMe_2)_4$ with cyclopentadiene produced mixtures of $Cp_2U(NMe_2)_2$ and $Cp_3U(NMe_2)$, a result of decomposition and rearrangement.

Given the success of preparing pure $Cp_2U(NEt_2)_2$, it was hoped that a similar result would be forthcoming utilizing $Th(NEt_2)_4$. This would have been very desirable since reactions to form Cp_2ThCl_2 were as unsuccessful as for Cp_2UCl_2. For instance, a reaction of $ThCl_4$ with two equivalents of NaCp produced mainly Cp_3ThCl. The synthesis of the intermediate $Th(NEt_2)_4$ required the use of a donor solvent like THF. When a preparation was attempted in pure hexane, it seemed that total conversion to $Th(NEt_2)_4$ had not occurred and that some intermediate chloro containing species were still present. A complication of the utilization of THF was the solubility of LiCl in the solvent hence it was necessary to either remove the THF solvent entirely or add a large amount of a hydrocarbon (hexane or pentane) to precipitate out the lithium chloride. Cyclopentadiene was added as a solution in THF at 0°C to the $Th(NEt_2)_4$ solution resulting in dark brown or dark orange-red solutions. Mass spectral and NMR analyses of the products of these reactions always showed mixtures of $Cp_2Th(NEt_2)_2$ and $Cp_3Th(NEt_2)$. As well the mass spectral data in particular indicated that bimetallic and other associated species may also have been present.

The highest purity obtained for a $Cp_2Th(NEt_2)_2$ synthesis was a ratio of 90:10 for $Cp_2Th(NEt_2)_2$ to $Cp_3Th(NEt_2)$. The preparation was done in THF and the LiCl was precipitated and removed only after the addition of cyclopentadiene. The result may seem a contradiction of the tendency of THF to promote disproportionation, however the improved yields of $Cp_2Th(NEt_2)_2$ in this case may simply reflect a lesser amount of decomposition resulting from a reduction in the required time for handling the compounds. Removing LiCl by filtration can be very slow and the chances of decomposition occurring at this point may be significant. The cyclopentadienyl substituted complexes are more stable than the tetrakisamides and can withstand better the necessary manipulations with less apparent decomposition.

The search for a precursor to Cp_2Th type chemistry was not pursued in order to concentrate on the reactivity of $Cp_2U(NEt_2)_2$. The very recent publication of the synthesis of $(Me_5C_5)_2ThCl_2$ [31] would seem to meet the requirement of a versatile reactive complex for Cp_2Th type compounds.

Preparation of $Cp_2U(NEt_2)_2$

The synthesis of $Cp_2U(NEt_2)_2$ is relatively straightforward, involving the *in situ* preparation of $U(NEt_2)_4$ as outlined below:

$$4LiNEt_2 + UCl_4 \longrightarrow U(NEt_2)_4 + 4LiCl \qquad (II-4)$$

$$U(NEt_2)_4 + 2CpH \longrightarrow Cp_2U(NEt_2)_2 + 2HNEt_2 \qquad (II-5)$$

Early preparations of $Cp_2U(NEt_2)_2$ suffered from the presence of large amounts (>20%) of $Cp_3U(NEt_2)$. There are a number of sources from which this compound may arise. The most obvious source would be the addition of greater than the required stoichiometric amount of cyclopentadiene in the second step since it has been found that this acid will displace an amide group from $Cp_2U(NEt_2)_2$ to form the tris(cyclopentadienyl) compound as in equation (II-6).[39]

$$Cp_2U(NEt_2)_2 + CpH \longrightarrow Cp_3U(NEt_2) + HNEt_2 \qquad \text{(II-6)}$$

To ensure that excess cyclopentadiene is not present, the correct amount of $U(NEt_2)_4$ should be available. The problem then becomes one of maximizing the purity and yield of $U(NEt_2)_4$. After a report[54] appeared mentioning the light sensitivity of thorium and uranium tetrakisdiethylamides, light was excluded from the reaction mixture by wrapping the flasks in foil paper. As mentioned previously, $U(NEt_2)_4$ is extemely air and moisture sensitive so manipulations were kept to a minimum. There are two synthetic procedures used to form $Cp_2U(NEt_2)_2$ from an *in situ* preparation of $U(NEt_2)_4$, dictated by the choice of solvent used. The first involved the simple addition of a THF solution of UCl_4 to a THF solution of $LiNEt_2$ cooled to 0°C. After reacting for a period of time, the solvent is removed, the resulting $U(NEt_2)_4$ is extracted with hexane or pentane and then subsequent reaction with cyclopentadiene is affected. As well, the reaction sequence of Edelstein *et al.*[49] can be followed. In this case, UCl_4 and $LiNEt_2$ are placed in a flask and the solvent Et_2O is condensed onto the solids. The LiCl precipitates out of solution and can be removed by filtration. The ether solvent must still be removed because a further step involving the crystallization of $Cp_2U(NEt_2)_2$ is not successful if an ether/pentane solvent mixture is employed. In both of the schemes outlined above heating the $U(NEt_2)_4$ reaction mixture or stirring it for longer than thirty hours lead to increased amounts of impurities and decomposition.

A complication of these reaction schemes is the fact that the actual amount of $U(NEt_2)_4$ formed cannot be measured. The isolation of pure $U(NEt_2)_4$ was then tried but the only time pure green crystals of $U(NEt_2)_4$ were isolated was from a preparation done in THF for a period of 24 hours. An attempted distillation at 90°C on the resultant green-black solid produced bright green crystals in a connecting tube. Various attempts to sublime the compound were hampered by severe splattering of the residue upon heating. Successful sublimation of $U(NEt_2)_4$ has been reported but the maximum yield was only 34.5%.[49]

In spite of these difficulties, the *in situ* preparation of $U(NEt_2)_4$ is satisfactory and produces fairly pure $Cp_2U(NEt_2)_2$ if the ratio of cyclopentadiene to the amide is kept to approximately 1.5. Table I is a summary of the different preparations of $Cp_2U(NEt_2)_2$ and outlines the effect of the various experimental conditions on yield and purity. A few trends are apparent. The solvent

Table I: Reaction Conditions for the Preparation of $Cp_2U(NEt_2)_2$.

No	Ratio $\frac{LiNEt_2}{UCl_4}$	Solvent	Reaction Time[a]	Ratio $\frac{CpH}{U(NEt_2)_4}$	Solvent	Reaction Time[b]	Yield[c] (%)	Amount Impurity $Cp_3U(NEt_2)$ (%)
1	4.04	THF	46 hrs	1.53	hexane	5 hrs	79.2	2.4
2	4.05	THF	26 hrs	1.40	pentane	3 hrs	71.0	<5
3	4.01	THF	30.5 hrs	1.82	pentane	3.5 hrs	76.3	9.5
4	4.0	THF	30 hrs	1.42	pentane	3.5 hrs	60.1	2.1
5	4.03	Et_2O	5 days	1.39	pentane	24 hrs	91.3	3.0
6	4.02	Et_2O	30 hrs	1.44	pentane	7 hrs	78.5	3.0
7	3.9	Et_2O	46 hrs	1.2	pentane	4 hrs	86.0	<5
8	4.1	Et_2O	26 hrs	1.9	pentane	3 hrs	80	6.1

[a] For equation (II-4).

[b] For equation (II-5).

[c] Based on amount of CpH used.

Et_2O appears to improve the yield of the reaction slightly. The most significant factor is the $CpH/U(NEt_2)_4$ ratio. A comparison of syntheses 3 and 4 shows an increase in the amount of $Cp_3U(NEt_2)$ detected when the ratio $CpH/U(NEt_2)_4$ is increased. The same effect is observed for syntheses 7 and 8. The length of time taken for the formation of $Cp_2(NEt_2)_2$ does not seem as important.

The presence of $Cp_3U(NEt_2)$ in all of the syntheses is in contrast to the pure $Cp_2U(NEt_2)_2$ reported by Jamerson.[29,39] Different technical ability may account for the discrepancy. In any case, for samples of $Cp_2U(NEt_2)_2$ containing less than 4.0% $Cp_3U(NEt_2)$ a simple procedure of dissolving the solid in hexane and filtering removes any impurities, as monitored by ^1H NMR. This situation is shown in Figure I for the solid from synthesis 6 which contained 3% $Cp_3U(NEt_2)$. An attempt to purify samples of $Cp_2U(NEt_2)_2$ by sublimation was not very successful. A small sample was heated to 105°C under mercury diffusion pump vacuum using a dry-ice cold finger. Very little sublimate was collected and upon raising the temperature slightly (108°C), the residue started to darken. The ^1H NMR spectrum of the sublimate showed only the peaks of $Cp_2U(NEt_2)_2$ although there were other impurities present in the sublimate which did not dissolve in the solvent (benzene) used. The residue showed peaks due to both $Cp_2U(NEt_2)_2$ and $Cp_3U(NEt_2)$. A sublimation

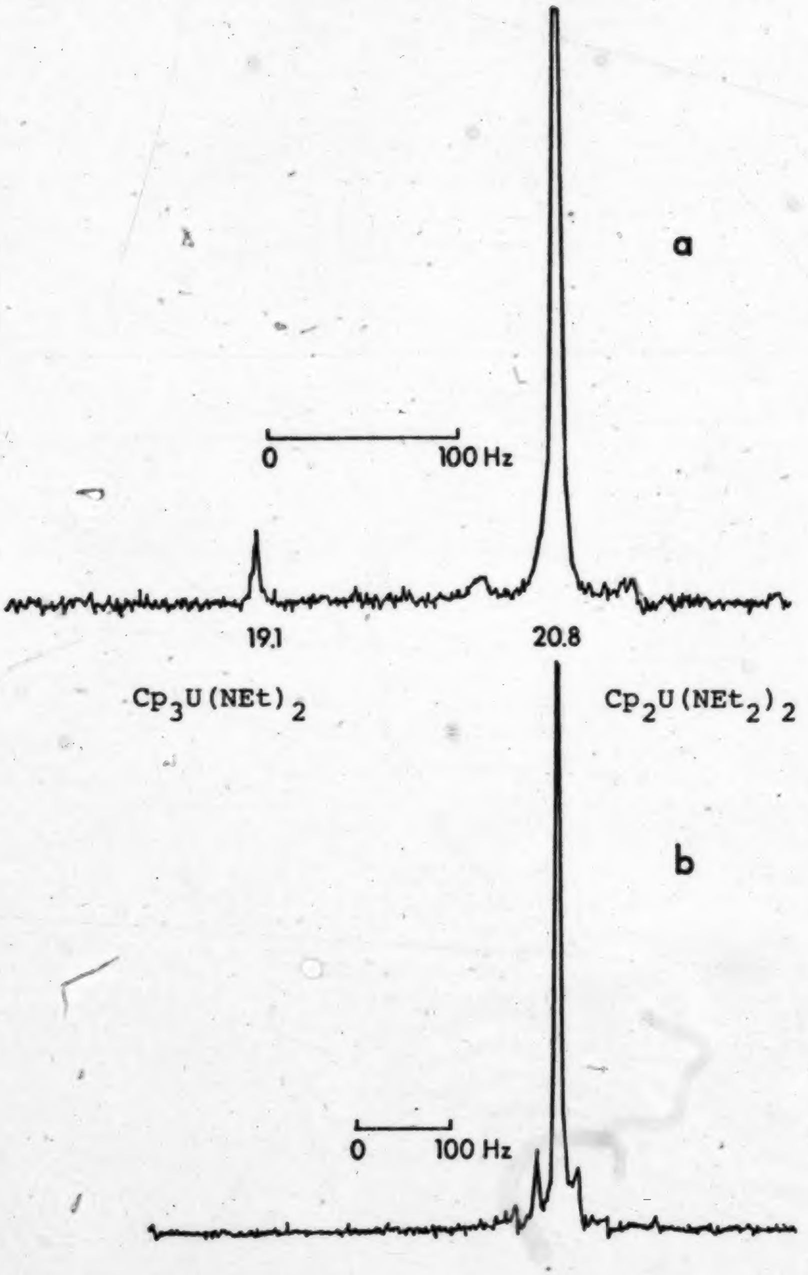

Figure I: ^{1}H NMR Spectra of the Cyclopentadienyl Resonance Region of $Cp_2U(NEt_2)_2$ and $Cp_3U(NEt_2)$.

[a] Initial solid in benzene-d_6, chemical shift in ppm from internal benzene. Temp = 35°C.

[b] Solid dissolved in hexane solution.

attempt by Reynolds and Edelstein at temperatures of around 120° and pressures of less than 10^{-4} mm produced mainly $Cp_3U(NEt_2)$.[55] Clearly sublimation is not a suitable route to a pure product.

Reactivity of $Cp_2U(NEt_2)_2$ Towards Other Amines

It has already been stated that the metal-nitrogen bond is reactive towards molecules containing acidic protons. This criterion can be extended to include other amines which are themselves weak acids. The aminolysis reaction is very common among the transition metal dialkyl-amides.[46] In organouranium chemistry, the transamination reaction has been used before as a useful synthetic route. For example, the compound $U(NPh_2)_4$ was produced by the following reaction.[50]

$$U(NEt_2)_4 + 4HNPh_2 \longrightarrow U(NPh_2)_4 + 4HNEt_2 \qquad (II\text{-}7)$$

These synthetic procedures can be extended to the compound $Cp_2U(NEt_2)_2$. It has been found that selected amines, more acidic than diethylamine, undergo a transamination reaction as shown in equation (II-8).

$$Cp_2U(NEt_2)_2 + xHNR_2 \longrightarrow Cp_2U(NEt_2)_{2-x}(NR_2)_x + xHNEt_2 \qquad (II\text{-}8)$$

$HNR_2 = HNPh_2,\ HNC_4H_4,\ HNC_4H_2Me_2,\ HNC_4Me_3(COOEt)$

$x = 1,2$

The driving force of the reaction is the difference in acidity indicated by the pKa values of HNR_2 and $HNEt_2$.

a) Diphenylamine, $HNPh_2$

The reaction of $Cp_2U(NEt_2)_2$ with two equivalents of diphenylamine in a hexane solvent at room temperature did not give the expected bis-substituted product, instead the mono-substituted compound precipitated out of solution as a microcrystalline red solid. Another reaction in benzene was stirred at room temperature for 5 days and then refluxed for 5 hrs. No precipitate was observed during this time, however upon concentration of the solution and after addition of hexane a red precipitate was obtained. A mass spectral analysis of this red solid indicated that a 50/50 mixture of $Cp_2U(NEt_2)(NPh_2)$ and $Cp_2U(NPh_2)_2$ was present. The bis-substituted product was not obtained from a THF solution either. Using an excess of diphenylamine in a THF solvent produced a mixture containing $Cp_2U(NPh_2)_2$, $Cp_2U(NEt_2)(NPh_2)$ and $CpU(NPh_2)_3$, but the main component was $Cp_3U(NPh_2)$. It is likely that some bis-substituted compound was formed but that rearrangement to $CpU(NPh_2)_3$ and $Cp_3U(NPh_2)$ occurred. The tendency of the THF solvent to cause rearrangements and further side products also occurs in reactions of transition metal amides.[56]

The apparent decrease in the reactivity of the second $U-NEt_2$ bond is interesting and may be due to the change in the strength of the uranium-nitrogen bonds. Since diphenylamine is a stronger acid than diethylamine, its conjugate base is weaker than the corresponding diethylamide moiety and would have a decreased tendency to donate the electron density of its nitrogen long pairs to uranium. As a result the metal can accept a greater amount of electron density from the nitrogen of the NEt_2 group forming a stronger $U-NEt_2$ bond in $Cp_2U(NEt_2)(NPh_2)$ than the U-N bond in $Cp_2U(NEt_2)_2$. Further substitution of the NEt_2 moiety is then more difficult. It must be recognized that the steric bulk of the NPh_2 group can also hinder further substitution. In hydrocarbon solvents the bis-substituted product is difficult to obtain because precipitation of the initially formed mono-substituted derivative effectively eliminates any further reaction.

A pure sample of $Cp_2U(NEt_2)(NPh_2)$ was produced from a reaction employing one equivalent of diphenylamine in a hexane solution. The compound was crystallized from a toluene/hexane solvent mixture. The ^1H-NMR spectrum is given in Figure II.

It is noted however that the compound $Cp_2U(NPh_2)_2$ has been synthesized[39] by reacting cyclopentadiene with tetrakis(diphenylamido)uranium(IV) as outlined in equation (II-9).

$$U(NPh_2)_4 + 2CpH \longrightarrow Cp_2U(NPh_2)_2 + 2HNPh_2 \qquad (II-9)$$

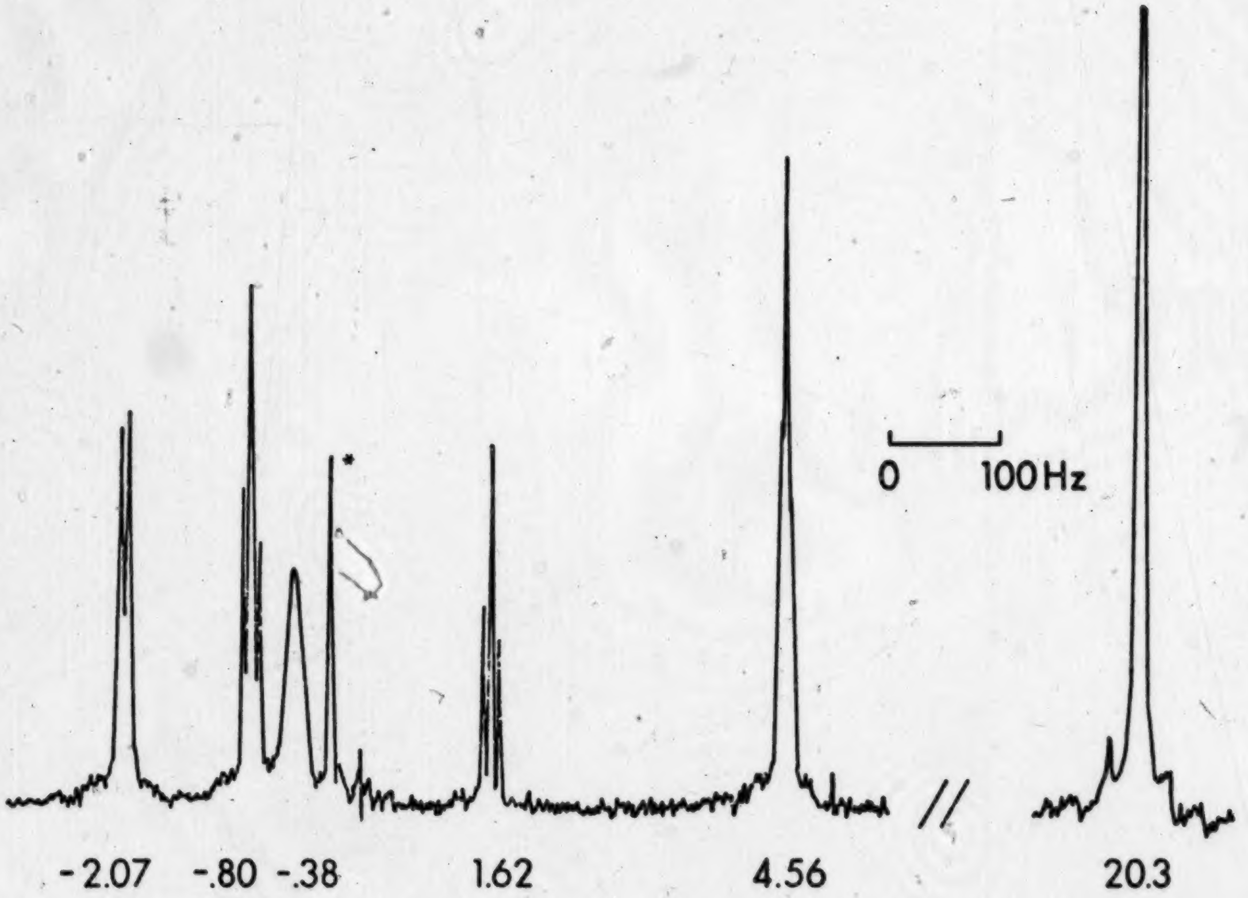

Figure II: ^{1}H NMR Spectrum of $Cp_2U(NEt_2)(NPh_2)$.

*Internal benzene, chemical shifts in ppm from this peak. Temp = 35°C.

b) Pyrroles, HNC_4H_4, $HNC_4H_2Me_2$, $HNC_4Me_3(COOEt)$

Three reactions of $Cp_2U(NEt_2)_2$ with pyrrole under varying conditions were attempted, but no pure products could be isolated. A reaction with two equivalents of pyrrole in the solvent THF produced mainly $Cp_3U(NC_4H_4)$, as determined from mass spectral data. An ^1H NMR spectrum of the gold-brown solid obtained from this reaction exhibited only one strong peak at 11.2 ppm above benzene. The reaction using two equivalents of pyrrole was then repeated in a hexane solvent which was stirred for 27 hours. The mass spectral data for the gold solid isolated indicated a mixture of $Cp_2U(NC_4H_4)_2$ and $Cp_3U(NC_4H_4)$. Another reaction of $Cp_2U(NEt_2)_2$ with one equivalent of pyrrole in hexane solvent for a reaction time of eleven hours produced a gold solid whose mass spectrum again indicated the presence of both $Cp_2U(NC_4H_4)_2$ and $Cp_3U(NC_4H_4)$. A ^1H NMR spectrum contained three peaks in the ratio 2.5:1:1 corresponding to the bis-substituted complex at 7.67 ppm, 14.9 ppm and 38.3 ppm above benzene, as well as a peak at 11.0 ppm for the Cp protons of $Cp_3U(NC_4H_4)$. The spectrum also had a few other smaller peaks from decomposition products. In comparing the two "hexane" reactions, the latter reaction with one equivalent of pyrrole produced more $Cp_2U(NC_4H_4)_2$ and less of the undesired $Cp_3U(NC_4H_4)$ than the former reaction which employed two equivalents of pyrrole. The presence of $Cp_3U(NC_4H_4)$ may be due to the ease with which pyrrole can change coordination mode from a σ-bonding amido group to a π-bonding ligand. This fluxionality has been studied by Marks *et al.*[13f,57] for the compound $U(NC_4H_2Me_2)_4$ whose variable temperature ^1H NMR pattern has been interpreted in terms of, among other processes, a rapid interconversion of the monohapto and pentahapto pyrrole rings. Such dynamic behavior coupled with a group transfer mechanism could produce the ten-coordinate $Cp_3U(NC_4H_4)$ species.

On the assumption that a more bulky ligand would result in the formation of only a single product, 2.4 equivalents of 2,5-dimethyl pyrrole were combined with $Cp_2U(NEt_2)_2$ in hexane solvent for a reaction time of 34 hours. Red crystalline material isolated from the reaction gave a mass spectrum which contained fragments from $Cp_2U(NEt_2)(NC_4H_2Me_2)$ and $Cp_3U(NEt_2)$. The ^1H NMR spectrum, Figure III, corroborates this assignment. (.16, s, Me; .67, q, CH_2; 5.96, t, CH_3; 19.8 s, H; 20.7, s, Cp of $Cp_2U(NEt_2)(NC_4H_2Me_2)$ and 8.3, t, CH_3; 19.1, s, Cp of $Cp_3U(NEt_2)_2$.) Hence the more bulky pyrrole, like diphenylamine, only replaces one diethylamide group, however in the pyrrole case it would seem that steric factors are controlling the course of the reaction.

That steric control does not always regulate this reaction is demonstrated in the case of an even bulkier

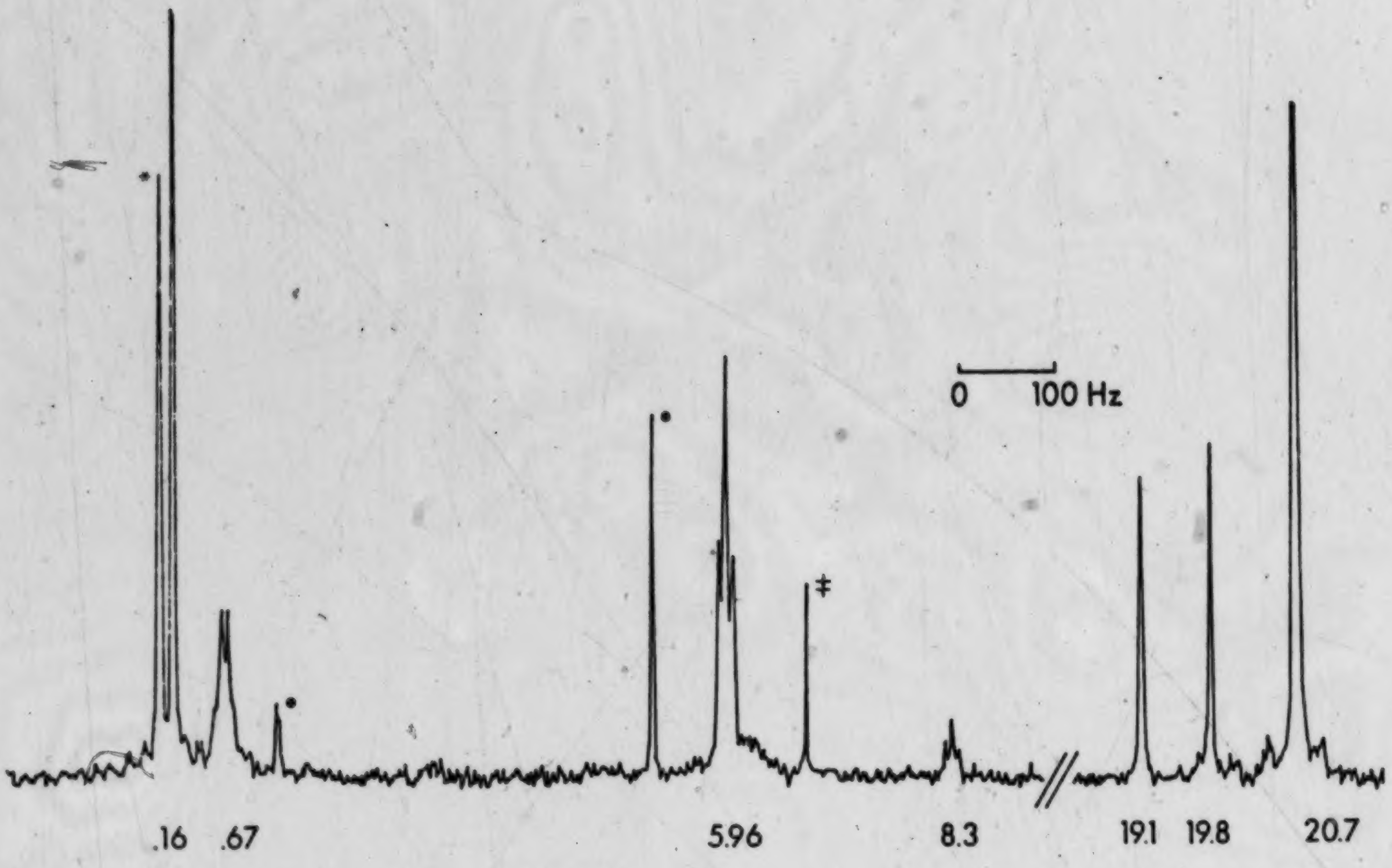

Figure III: ^{1}H NMR Spectrum of $Cp_2U(NEt_2)(NC_4H_2Me_2)$ and $Cp_3U(NEt_2)$ Mixture.

*Internal benzene, chemical shifts in ppm from this peak, •decomposition, ‡grease.

Temp = 35°C.

pyrrole, ethyl 3,4,5-trimethylpyrrole 2-carboxylate. A reaction of 1.82 equivalents of this pyrrole and $Cp_2U(NEt_2)_2$ in a hexane solvent for a reaction time of 24 hours produced the bis-substituted species. There was no evidence for the mono-substituted compound in the mass spectrum. The ^1H NMR spectrum of $Cp_2U[NC_4Me_3(COOEt)]_2$ is shown in Figure IV. The ethyl resonances have been shifted considerably upfield which suggests that the carbonyl oxygen is coordinating to the uranium centre. This extra interaction would explain the formation of the bis-substituted complex,as for this complex electronic factors predominate over steric concerns.

Discussion of ^1H NMR Spectral Data

The chemical shifts observed in the ^1H NMR spectra of the uranium amides in deuterated benzene solvent are given in Table II. The resonances are shifted considerably from the positions normally expected for organic moieties. Such shifts are not unexpected for compounds containing a paramagnetic centre, which in this case is the uranium(IV), $5f^2$, metal ion. Large paramagnetic chemical shifts are the result of both contact and pseudo-contact contributions.[58] The pseudo-contact or dipolar term contains a geometrical expression $(3 \cos^2 \Theta - 1)/r^3$ so that in some cases, where the contact contribution to the isotropic shifts remains approximately

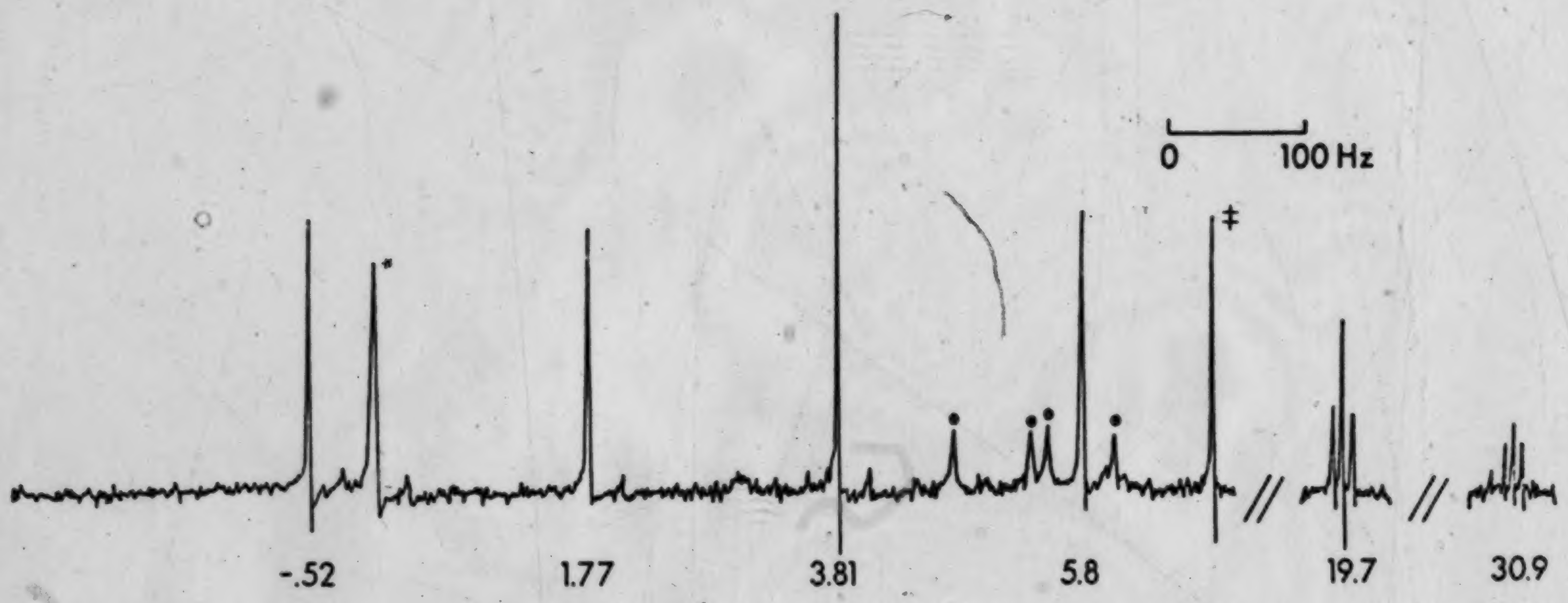

Figure IV: ^{1}H NMR Spectrum of $Cp_2U[NC_4Me_3(COOEt)]_2$.

*Internal benzene, chemical shifts in ppm from this peak. Temp = 35°C.

‡grease. •decomposition.

Table II: ^1H NMR Data of Amide Derivatives of Uranium(IV).

	Resonances[a,d]					
	Cp	CH_3 of NEt_2	CH_2 of NEt_2	Aromatic	Pyrrole	Ref.
$Cp_2U(NEt_2)_2$[e]	20.94,s	5.70,t	-1.54,q			c
$Cp_2U(NPh_2)_2$[f]	25.45,s			1.70,d(o);0.72,t(m) 4.02,t(p)		39
$Cp_2U(NEt_2)(NPh_2)$[e]	20.3,s	4.56,t	-.38,q	-2.07,d(o);-.80,t(m) 1.62,t(p)		c
$U(NEt_2)_4$[b,g]		12.6	-5.8			59
$U(NPh_2)_4$[f]				8.32(o);2.30(m) 4.42(p)		39
$Cp_2U(NEt_2)(NC_4H_2Me_2)$[e]	20.7,s	5.96,t	.67,q		.16,s(Me);19.8,s(H)	c
$Cp_2U[NC_4Me_3(COOEt)]_2$[e]	3.8,s				-.52,s(Me);1.77,s(Me);5.80,s(Me) 19.7,t(CH_3);30.9,q(CH_2)	c

[a] ppm relative to internal benzene,positive number indicate shift is to high field.

[b] Chemical shifts recalculated relative to internal benzene.

[c] This work.

[d] Key: s = singlet, d = doublet, t = triplet, q = quartet, o = ortho, m = meta, p = para.

[e] Temp = 35°C. [f] Temp = 44°C. [g] Temp = 24°C.

constant, it is possible to correlate ^{1}H NMR data and gross structural features. Marks *et al.*[10] have suggested that the constancy of the chemical shift of the Cp protons in a series of Cp_3UR compounds may be a result of similar molecular magnetic anisotropy resulting from comparable structures. The similarity in the chemical shifts of the Cp protons for all the bis(cyclopentadienyl) derivatives, except the carboxylate substituted pyrrole compound, is perhaps an indication that the tetrahedral-type structure usually found for Cp_2ML_2 (M = transition metal, L = monodentate ligand) type compounds is also possessed by the present complexes. The fact that the peak position of the Cp resonance for the compound $Cp_2U[NC_4Me_3(COOEt)]_2$ is considerably different than the other derivatives again suggests that the coordination about the uranium centre may include interaction with the carbonyl oxygens. As mentioned before this assumed interaction is further supported by the large shifts observed for the methylene and methyl moieties of the carboxylate group.

Discussion of Mass Spectral Data

The mass spectral data for $Cp_2U(NEt_2)(NPh_2)$ is given in Table III, along with data for $Cp_2U(NEt_2)_2$ and $Cp_2U(NPh_2)_2$ which have been included for comparative purposes. The mass spectrum and major fragmentation

Table III: Mass Spectra[a] of $Cp_2U(NEt_2)_2$, $Cp_2U(NPh_2)_2$ and $Cp_2U(NEt_2)(NPh_2)$.

Assignment	$Cp_2U(NEt_2)_2$[b,c]		$Cp_2U(NPh_2)_2$[d,e]		$Cp_2U(NEt_2)(NPh_2)$[f]	
	m/e	rel.abund (%)	m/e	rel.abund (%)	m/e	rel.abund (%)
$Parent^+$	512	40	704	8	608	60.5
$Parent\text{-}Cp^+$	447	.4	639	.9	543	.5
$Cp_2U(NEt_2)^+$	440	11			440	28.4
$Cp_2U[(NEt)(C_2H_4)]^+$	439	21			439	18.2
$Cp_2U[(NEt)(C_2H_3)]^+$	438	100			438	100
$Cp_2U[N(C_2H_3)_2]^+$	436	10			436	31.8
$Cp_2U(NPh_2)^+$			536	100	536	60.9
$CpU(NPh_2)^+$			471	1.8	471	5.7
$CpU[(NPh)(C_6H_4)]^+$			470	6.0	470	10.1
$CpU[N(C_6H_4)(C_6H_3)]^+$			468	9.2	468	10.7
$Cp_2U(NPh)^+$			459	1.9	459	1.4
$Cp_2U(C_6H_4)^+$			444	3.0	444	3.6
$CpU(NPh)^+$			394	7.2	394	11.7
Cp_2U^+	368	77	368	24.8	368	78.5
CpU^+	303	19	303	2.4	303	9.1

[a] Not corrected for ^{13}C. [b] Taken from Ref. 39. [c] Temp = 105°C.

[d] Taken from private communication, J. Jamerson. [e] Temp = 210°C.

[f] Temp = 115°C.

processes of $Cp_2U[NC_4Me_3(COOEt)]_2$ are summarized in Table IV. The mass spectral data for $Cp_2U(NEt_2)(NC_4H_2Me_2)$ and $Cp_2U(NC_4H_4)_2$ have not been included since these products were not obtained pure, although some information was gathered. The most apparent trend among the compounds is that for $Cp_2U(NPh_2)_2$ and $Cp_2U(NC_4H_4)_2$, the base peak is $Cp_2U(NR_2)^+$, while for $Cp_2U(NEt_2)_2$ and $Cp_2U(NEt_2)(NPh_2)$ the ion $Cp_2U[NEt(C_2H_3)]^+$ predominates. For the compound $Cp_2U(NEt_2)(NC_4H_2Me_2)$ the most intense peak is for the fragment Cp_2U^+, but the next intense peak is caused by $Cp_2U[NEt(C_2H_3)]^+$. Clearly the uranium-nitrogen bond undergoes more facile cleavage than the uranium-cyclopentadienyl bond. This pattern is different than the fragmentation behavior of the inserted compounds, $Cp_2U(XYCNEt_2)_2$ or the carboxylate compounds, $Cp_2U(XYCR)_2$ discussed in later chapters. These latter complexes, like $Cp_2U[NC_4Me_3(COOEt)]_2$, exhibit base peaks corresponding to cleavage of the uranium-Cp bonds. It would seem that uranium-nitrogen bonds which are unsupported (no interaction of the metal centre with a functional group on the ligand) are more easily broken. The mass spectral behavior of the compound $Cp_2U[NC_4Me_3(COOEt)]_2$ is consistent with the suggestion that there is involvement of the ethyl carboxylate group with the uranium centre.

An analysis of the fragmentation pattern of $Cp_2U(NEt_2)(NPh_2)$ indicates that the uranium-diphenylamide

Table IV: Mass Spectrum of $Cp_2U[NC_4Me_3(COOEt)]_2$ and Major Fragmentation Processes.

m/e	Relative Abundance[a,b] (%)	Assignment
728	18.3	$Cp_2U[NC_4Me_3(COOEt)]_2^+$
663	100	$CpU[NC_4Me_3(COOEt)]_2^+$
549	3.8	$Cp_2U[NC_4Me_3(COOEt)]H^+$
528	57.7	$CpU[NC_4Me_3(COOEt)](OEt)^+$
413	5.2	$Cp_2U(OEt)^+$
393	23.1	$CpU(OEt)_2^+$
384	3.7	Cp_2UO^+
368	1.0	Cp_2U^+
364	11.5	$CpU(OEt)(O)^+$

Process	Metastable Peaks Calcd.	Obs.
$Cp_2U[NC_4Me_3(COOEt)]_2^+ \longrightarrow CpU[NC_4Me_3(COOEt)]_2^+$	603.8	604
$CpU[NC_4Me_3(COOEt)]_2^+ \longrightarrow CpU[NC_4Me_3(COOEt)](OEt)^+$	420.5	421
$CpU[NC_4Me_3(COOEt)](OEt) \longrightarrow CpU(OEt)_2^+$	292.5	293

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[a] 90°C.

[b] Not corrected for ^{13}C.

bond is more easily cleaved than the uranium-diethylamide bond. Since the NPh_2 ligand is less of a π-donating ligand than NEt_2, it is not unexpected that the uranium-NPh_2 interaction is weaker than the uranium-NEt_2 interaction.

Discussion of Infrared Spectral Data

The characteristic infrared frequencies in the 1600-400 cm^{-1} region for $Cp_2U(NEt_2)_2$, $Cp_2U(NPh_2)_2$ and $Cp_2U(NEt_2)(NPh_2)$ are listed in Table V. The infrared spectra of $Cp_2U(NC_4H_4)_2$ and $Cp_2U(NEt_2)(NC_4H_2Me_2)$ were not obtained because of the mixtures of compounds present in the preparations. An infrared spectrum of $Cp_2U[NC_4Me_3(COOEt)]_2$ was recorded however the sample hydrolyzed during mull preparation. The discussion will hence centre on the first three compounds.

The assignment of the bands due to the cyclopentadienyl moiety is based on other organouranium compounds, mainly those of the type Cp_3UR. A recent analysis of the vibrational spectra of compounds containing the η^5-cyclopentadienyl ligand has shown that the majority of the Cp-ligand frequencies do not vary significantly.[60] It has been tacitly assumed that the cyclopentadienyl rings are bonded to the uranium in a symmetrical, pentahapto fashion. It is clear, based on the simple infrared pattern of the Cp group,[60,61] that this assumption is

Table V: Characteristic Infrared Absorptions for $Cp_2U(NR_2)_2$ Complexes[a,b]

$Cp_2U(NEt_2)_2$[c]	$Cp_2U(NPh_2)_2$[c]	$Cp_2U(NEt_2)(NPh_2)$	Assignment
		1595s	
		1583m	ν_{C-C} phenyl
		1564m	
1439m			ν(C-C) of Cp
1145s	1146m	1180m	asym $\nu(NC_2)$
		1147m	
	1096s,br		
1012s	1016s	1011m	δ(C-H) of Cp
994s			sym $\nu(NC_2)$
768vs	802vs	783s	γ(C-H) of Cp
	778sh	749s	δ(C-H) phenyl
	747m	693s	
	725s		
561m		494m	ν(M-N)
494m			

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[a] In cm^{-1}, in Nujol and Fluorolube mulls.

[b] s-strong, vs-very strong, m-medium, br-broad, sh-shoulder.

[c] From ref. 39.

correct. The sharp singlets observed for the Cp groups in the ^1H NMR spectra are of course also consistent with this. The Cp bands in the fingerprint region that are easily identifiable are the in-plane , δ(C-H), and out-of-plane, γ(C-H), deformation modes of the Cp ring. A short list of uranium compounds and the positions of these bands are given in Table VI.

Unfortunately, for the $Cp_2U(NR_2)_2$ compounds, the amide group also has important infrared modes which absorb in the same regions as the Cp group. The in-plane deformation mode and the symmetric stretch of the NC_2 group appear in approximately the same position, 990 to 1020 cm^{-1}, although it seems from a comparison to other Cp-Metal derivatives that the δ(C-H) mode of the cyclopentadienyl ligand comes at the higher end of the region indicated. The out-of-plane deformation mode of the Cp group and an unassigned NEt_2 peak also come in the same region. For the diphenylamide compounds, a further complication are peaks resulting from the phenyl ring. The metal-nitrogen stretch assignments, ν(M-N), are in the region generally found for pyrrole and indole derivatives of Cp_2Ti and Cp_2Zr type compounds.[63] The positions and intensities of some of the characteristic cyclopentadienyl bands have been utilized previously to assess the nature of the M-Cp bond. The band that is normally monitored is the γ(C-H) mode around 800 cm^{-1},

Table VI: Selected Bands[a] in the Infrared Spectra of Cp-containing Compounds.

Compound	δ(C-H)Cp	γ(C-H)Cp	Ref.
$Cp_3U(C{\equiv}CH)$	1012 vs	811,792,779vs,br	62
$Cp_3U(C_5H_4)Fe(C_5H_5)$	1017 vs	816,797,778s,br	62
$Cp_3U(C_4H_9)$	1016 s	807,780vs	10
$Cp_3U(CH_2CMe_3)$	1010 s	780vs	10
$Cp_3U(NEt_2)$	1014 s	808s	39

[a] Given in cm^{-1}.

which according to Fritz,[60] shifts to lower frequencies as the ionicity of the metal-Cp bond increases. For the present set of compounds this band shifts from 768 cm^{-1} for $Cp_2U(NEt_2)_2$ to 783 cm^{-1} for $Cp_2U(NEt_2)(NPh_2)$ and then to 802 cm^{-1} for $Cp_2U(NPh_2)_2$ indicating that replacing the diethylamide group with the less π-donating diphenylamide ligand produces more covalent cyclopentadienyl-uranium bonds. This would be expected, for as the amount of electron density transmitted by the amide groups to the metal centre decreases, there is an increased interaction between the metal and cyclopentadienyl ligand to compensate for the reduced electron density on the metal.

Conclusions

The tetrakisamide compounds of uranium have been shown to be useful precursors for the synthesis of Cp_2-$U(NR_2)_2$ complexes. However the considerable air and moisture sensitivity of $U(NR_2)_4$ species does limit their further synthetic utility. The relatively facile preparation of $Cp_2U(NEt_2)_2$ from the corresponding amide is significant since this compound possesses labile uranium-nitrogen bonds. The reactions of $Cp_2U(NEt_2)_2$ with a variety of amines were shown to be controlled by mainly steric factors. The bulkier the amide group the more likely the formation of the mono-substituted derivative would occur. In one case, however, it was shown that when the amine contained a functional group which could interact with the metal, the propensity of uranium to achieve high coordination did outweigh steric considerations and the bis-substituted derivative was obtained.

CHAPTER THREE

CARBAMATE DERIVATIVES OF BIS(CYCLOPENTADIENYL)URANIUM(IV)

Introduction

The reactivity of the metal nitrogen bond in uranium and thorium tetrakisamides towards amines in transamination reactions was investigated in the preceding chapter. The reactions were similar to those exhibited by the early transition metal amides. These transition metal amides also undergo insertion reactions with molecules containing polar multiple bonds. The most common reagents have been CO_2, CS_2, and COS which form various carbamato-type species. These compounds have been widely studied because of their ability to stabilize metal centres in unusual oxidation states.[64]

Insertion of CX_2 (X = O, S, Se) into the metal-nitrogen σ-bonds of the tetrakisamide actinide (IV) complexes has been described by Bagnall and Yanir[65] as a means of obtaining thorium and uranium carbamates. Dithiocarbamate complexes of thorium and uranium have been prepared before, but the synthetic method involved the use of the metal chlorides and sodium salt.[66] It was expected that the reagent $Cp_2U(NEt_2)_2$ would react in a similar manner as $U(NEt_2)_4$ with CS_2, COS and CO_2 to give insertion-type compounds of the formula $Cp_2U(XYCNEt_2)_2$ (X, Y = O or S and X = O, Y = S). A preliminary study of the reactivity of $Cp_2U(NEt_2)_2$ with

CS_2 indicated that a very facile insertion of the CS_2 molecule into the uranium-nitrogen bond was occurring.[39]

Synthetic Aspects and Physical Properties

Hydrocarbon solutions of $Cp_2U(NEt_2)_2$ react rapidly with CO_2, CS_2 and COS to give the corresponding carbamates according to the reaction (III-1):

$$Cp_2U(NEt_2)_2 + 2CXY \longrightarrow Cp_2U(XYCNEt_2)_2 \qquad \text{(III-1)}$$

In cases where excess reagent, CXY, is used the insertion occurs only into the uranium-nitrogen bonds. The reactions are quite rapid and give almost quantitative yield of the anticipated product. The cyclopentadienyl ring in the formed carbamates retains its pentahapto bonding mode as determined by the characteristic bands for a η^5-C_5H_5 ring seen in the IR spectra of the complexes.[61] The observation of a single sharp line, assignable to the cyclopentadienyl protons in the ^{1}H NMR spectra is also consistent with this formulation. Molecular weight determinations show that both $Cp_2U(S_2CNEt_2)_2$ and $Cp_2U(OSCNEt_2)_2$ are monomeric in benzene, the variable results obtained for $Cp_2U(O_2CNEt_2)_2$ however indicated polymeric behavior which is both solvent and concentration dependent. Although the apparent high degree of polymerization (trimer to a dodecamer) found for $Cp_2U(O_2CNEt_2)_2$ in benzene compared to the other inserted products is surprising, the tendency for association is nevertheless as expected based on the variations in the ligands bite sizes; carbamate < thiocarbamate < dithiocarbamate.[67] Of course, aggregate formation in carbamate complexes has been seen before. Examples are provided by the monothiocarbamates of the late transition metals,[68] $M(OSCNR_2)$ (M = Cu, Ag; R = alkyl), and by the tin carbamate complex, $Me_3Sn(O_2CNMe_2)$.[69,70]

The mass spectra of the three compounds and their major fragmentation patterns are given in Tables VII and VIII. The results indicate that $Cp_2U(S_2CNEt_2)_2$ and $Cp_2U(OSCNEt_2)_2$ are monomeric in the gas phase as well, attempts to observe polymeric fragments for $Cp_2U(O_2CNEt_2)_2$ by varying the probe temperature met with failure. The mass spectral assignments are speculative since they are not confirmed by high resolution data, however the assignments are chemically reasonable. The parent ion is observed in all three cases in approximately the same relative abundance. There appears to be a slight amount of thermal disproportionation occurring, since very small amounts (less than 1%) of $CpU(X_2CNEt_2)_3$ and $Cp_3U(X_2CNEt_2)$ appear in the mass spectra. These, however, are not observed in the NMR spectra of the compounds. In addition elemental analyses indicate pure compounds.

The major breakdown from the parent ion involves loss of a cyclopentadienyl moiety. The loss of a carbamate ligand is a much less favorable process. Another major

Table VII. Mass Spectral Data for $Cp_2U(XYCNEt_2)_2$[a] Complexes.

Assignment	$Cp_2U(S_2CNEt_2)_2$[b]		$Cp_2U(OSCNEt_2)_2$[c]		$Cp_2U(O_2CNEt_2)_2$[d]	
	m/e	rel. abundance (%)	m/e	rel. abundance (%)	m/e	rel. abundance (%)
P^+	664	20.6	632	25.6	600	23.2
$[P-Cp]^+$	599	100	567	100	535	100
$[P-Cp-H_2CXY]^+$	521	18.6	505	18.2	489	29.0
$[P-(XYCNEt_2)]^+$	516	13.4	500	4.0	484	12.0
$[P-Cp-(XYCNEt_2)]^+$	451	12.4	435	11.6	419	13.4
$[CpU(NEtC_2H_3)_2]^+$	443	.2	443	.6	443	19.4
$[Cp_2U[NEt(C_2H_3)]^+$	438	2.0	438	1.4	438	4.8
Cp_2U	368	7.2	368	2.5	368	7.4
$CpUS_2$	367	21.6	367	1.2	367	-
CpUSH	336	10.3	336	-	336	-
CpUS, $CpUO_2$	335	22.7	335	4.0	335	.1
CpUOH	-	-	320	.9	320	1.2
CpUO	-	-	319	11.6	319	15.2

[a] Not corrected for ^{13}C. [b] Temp = 160°C. [c] Temp = 100°C. [d] Temp = 100°C.

Table VIII. Major Fragmentation Processes for $Cp_2U(XYCNEt_2)_2$ Complexes.

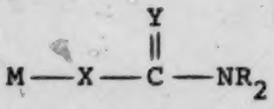
Process	Metastable Peaks CS_2[a] Calcd	Obs	COS[b] Calcd	Obs	CO_2[c] Calcd	Obs
$Cp_2U(XYCNEt_2)_2^+ \rightarrow CpU(XYCNEt_2)_2^+ + Cp$	540.4	541	508.7	509	477.0	477.2
$CpU(XYCNEt_2)_2^+ \rightarrow CpU(XYCNEt_2)(NEtC_2H_3)^+ + H_2CXY$	453.2	453.5	449.8	450	447.0	447
$CpU(XYCNEt_2)(NEtC_2H_3)^+ \rightarrow CpU(NEtC_2H_3)_2^+ + H_2CXY$			388.6	389	401.3	401.5
$\rightarrow CpU(XYCNEt_2)^+ + NEtC_2H_3$	390.4	391	374.7	374.9		

[a] $Cp_2U(S_2CNEt_2)_2$. [b] $Cp_2U(OSCNEt_2)_2$. [c] $Cp_2U(O_2CNEt_2)_2$.

fragmentation mode is loss of H_2CXY, being most facile in the carbamate complex. A comparison of transition metal tris(dialkyldithiocarbamate) complexes to the uranium compounds indicates that loss of S_2CNR_2 is more significant in the former.[71] This observation may suggest that a ligand will be lost to decrease steric congestion around the transtion metal. For the uranium compounds the U-Cp bond is more easily broken.

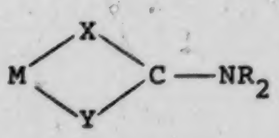
Coordination Mode of the Carbamate Moieties

The great interest in carbamate complexes is a result of some unique characteristics of the R_2NCX_2 ligand. This moiety can bond in a variety of fashions (1, 2, 3, 4), the most common modes being either 1 (monodentate) or 2 (terminal bidentate).

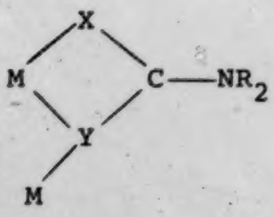


$M-X-\overset{\overset{\displaystyle Y}{\|}}{C}-NR_2$

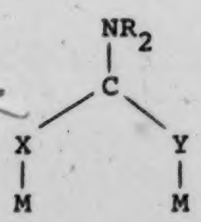
1



2



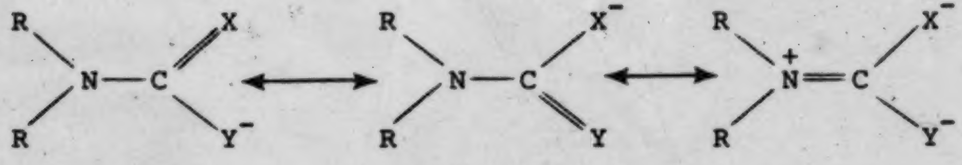
3



4

Crystal structure determinations of a number of dithiocarbamate and monothiocarbamate complexes have shown all four bonding modes. The compound $Sn(S_2CNEt_2)_4$[72] possesses two terminal bidentate and two monodentate ligands. Another compound containing mixed coordination modes is $[Ru(NO)(S_2CNMe_2)_3]$[73] which has one monodentate dithiocarbamate and two terminal bidentate moieties. The ligating mode 3 is observed in the iron dimer $[Fe(S_2CNEt_2)_2]_2$[74] where each iron is bonded to a bridging sulfur atom which itself is part of a terminal bidentate ligand. The hexameric structure of $[AgSOCN(iPr)_2]_6$ also involves bonding of type 3.[75] Simple bridging mode 4 has been established for instance in $Zn(S_2CNEt_2)_2$[76] and $U_4O_2(O_2CNEt_2)_{12}$.[77]

In the absence of structural information the infrared spectra of these complexes proved to be valuable, although not infallible, in distinguishing between the monodentate and bidentate bonding modes of the carbamate moieties. In the case of a dithiocarbamate ligand, the criteria for monodentate coordination has been the presence of two $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ and two $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ absorptions around 1500 and 1000 cm^{-1} respectively.[78,79] The bidentate moiety exhibits single $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ bands where the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching frequency is in the range of 1480-1550 cm^{-1}. A rationale for the variable position of this absorption is easily obtained by making reference to the possible resonance structures of the carbamate ligands, 5a-c. Increased importance of form 5c is seen to cause a concomitant increase



5a 5b 5c

in $\nu(C\overset{\cdots}{-}N)$. The value of the $C\overset{\cdots}{-}N$ stretching frequency has been correlated with the nature of the substitutents R on the nitrogen atom of the carbamate ligand and with that of the ancillary ligands on the central metal atom. The $\nu(C\overset{\cdots}{-}S)$ stretching frequency is not as sensitive to differing R groups.[80] Structural determinations of $UO_2(S_2CNEt_2)_2L$ where L = Ph_3AsO and Ph_3PO show bidentate dithiocarbamate groups. The infrared data gave $\nu(C\overset{\cdots}{-}N)$ values of 1480 cm^{-1} (Ph_3AsO) and 1479 cm^{-1} (Ph_3PO) and $\nu(C\overset{\cdots}{-}S)$ values of 995 cm^{-1} and 992 cm^{-1}, respectively.[81] X-ray analysis of the compounds $Ti(S_2CNEt_2)_4$[82] and $Ti(S_2CNMe_2)_3Cl$[83] have shown that both possess bidentate dithiocarbamate groups. These complexes exhibit a single $\nu(C\overset{\cdots}{-}N)$ band at 1493[78] and 1526 cm^{-1},[84] respectively, however the latter also has two $\nu(C\overset{\cdots}{-}S)$ bands at 990 and 981 cm^{-1}.[84] Fay *et al.*[85] have noted that sometimes two $\nu(C\overset{\cdots}{-}N)$ bands are observed even though an X-ray analysis has shown bidentate coordination. They suggest that in most monodendate coordination systems, the two $\nu(C\overset{\cdots}{-}N)$ bands are separated by greater than 20 cm^{-1}. The same argument could hold for the $\nu(C\overset{\cdots}{-}S)$ stretch region also.

For monothiocarbamate complexes, bidentate coordination has been associated with $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ values between 1500-1580 cm^{-1} and a strong $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band around 1500-1550 cm^{-1} as in the dithiocarbamate case. The bidentate monothiocarbamate complex $\mathrm{Ti(OSCNEt_2)_4}$ has $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ bands at 1547 and 1530 cm^{-1} respectively[86] and similarly $\mathrm{Fe(SOCNMe_2)_3}$ exhibits bidentate coordination[87] and has a $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ band at 1540 cm^{-1}.[88] Examples of monodentate coordination are the compound $\mathrm{Pd(PPh_3)(SSeCNMe_2)(SOCNMe_2)}$ which has a $\nu(\mathrm{C{=}O})$ band around 1600 cm^{-1} [89] and $\mathrm{Me_3Sn(OSCNMe_2)}$ with a band at 1621 cm^{-1}.[70]

Chisholm and Extine have studied a series of carbamato compounds quite extensively and have determined, through an analysis of infrared and structural data, that a strong band in the region of 1550-1600 cm^{-1} would be characteristic of a $\nu(\mathrm{O_2CN})$ for a bidentate ligand.[67a,90] The compound $\mathrm{Ti[O(iPr)]_3(O_2CNEt_2)}$ is also assumed to have a bidentate ligand based on an infrared spectrum that shows strong bands at 1560-1475 cm^{-1}.[91] A monodentate carbamate group has a $\nu(\mathrm{O_2CN})$ band above 1620 cm^{-1} as in the species $\mathrm{W(NMe_2)_3(O_2CNMe_2)_3}$ which has a band at 1636 cm^{-1}.[90]

Characteristic infrared frequencies for the new cyclopentadienyl uranium carbamates are listed in Table IX. Based on the foregoing literature survey the data are clearly consistent with a bidentate bonding mode of the carbamate ligands in these molecules. Further

Table IX. Characteristic Infrared Absorptions of $Cp_2U(XYCNEt_2)_2$ Complexes (cm^{-1})[a]

	$Cp_2U(S_2CNEt_2)_2$	$Cp_2U(OSCNEt_2)_2$	$Cp_2U(O_2CNEt_2)_2$
ν(OCN)		1537 m	1549 m
		1521 m	1512 s
		1514 m	1503 s
ν(C-N)	1484 s		
δ(C-H)Cp	1017 m	1019 m	1030 m
	1012 m		
ν(C-S)	915 m	946 w	
γ(C-H)Cp	805 sh	791 vs	796 sh
	792 vs	783 vs	785 vs

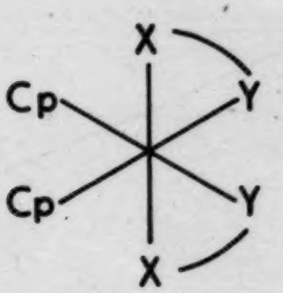
[a] In Nujol and Fluorolube mulls.

corroboration of this point comes from a comparison of the present results with those of other carbamate complexes of uranium where bidentate behavior of the ligands was also suggested or, as is the case with $U(S_2CNEt_2)_4$, conclusively established by X-ray structure determination.[92] The observed values are 1494 and 996 cm^{-1} for $\nu(C\overset{\cdots}{-}N)$ and $\nu(C\overset{\cdots}{-}S)$ in $U(S_2CNEt_2)_4$,[65] 1515-1520 cm^{-1} for $\nu(OCN)$ in $U(OSCNEt_2)_4$,[65] and 1510 cm^{-1} for $\nu(OCN)$ in $U(O_2CNEt_2)_4$.[65,93] With the exception of $\nu(C\overset{\cdots}{-}S)$ these frequencies are indeed rather similar to the values listed in Table IX. No special significance is to be attached to the discrepancy in $\nu(C\overset{\cdots}{-}S)$ since due to an absorption from the Cp ligand system in the 1000 cm^{-1} region the assignment of the $\nu(C\overset{\cdots}{-}S)$ is the least secure in the present compounds. Of course the bidentate bonding mode of the carbamate ligand is also consistent with the known preference of uranium for high coordination number. The increase in formal coordination number on going from the starting material to final products could in fact account in part for the observed enhanced stability of the $Cp_2U(XYCNEt_2)_2$ complexes over $Cp_2U(NEt_2)_2$. The ability of the metal to achieve high coordination number almost seems to be a prerequisite for the formation of this type of compound. Indeed, whereas transition metals are known to form a plethora of Cp_2ML_2 derivatives containing monodentate ligands,[94] complexes with two pentahapto cyclopentadienyl ligands in conjunction with two bidentate ligands are conspicuous by their absence. $(MeCp)_2Hf(BH_4)_2$[95] appears to be the only transition metal example so far identified.

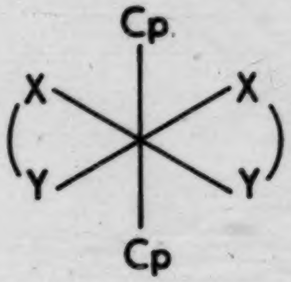
The other frequencies listed in Table IX are characteristic of the cyclopentadienyl moiety. The appearance of only a few bands assignable to this group is consistent with the presence of η^5-C_5H_5 rings.[61,96] As mentioned in the previous chapter, the out-of-plane deformation mode, γ(C-H) around 800 cm^{-1} has been used to draw conclusions about the nature of the M-Cp bond. The γ(C-H) value for the carbamate complexes decreases from 792 cm^{-1} for $Cp_2U(S_2CNEt_2)_2$, to 787 cm^{-1} (average) for $Cp_2U(OSCNEt_2)_2$ and 785 cm^{-1} for $Cp_2U(O_2CNEt_2)_2$. These values are higher than the value of ~770 cm^{-1} for $Cp_2U(NEt_2)_2$. Within the series, it seems that complexes with oxygen-containing ligands have more ionic uranium-cyclopentadienyl bonds. This same trend is observed for the carboxylate complexes discussed in the succeeding chapter.

Coordination Geometry

Closely connected to the bonding modes of the ligands in these complexes is the coordination geometry about the central uranium atom. A commonly used practice in describing the basic geometry of Cp_xML_n type compounds is to count the Cp ligands as occupying one coordination site. With this convention the compounds can be considered as pseudo-six-coordinate molecules. The basic geometry for six-coordination is octahedral and within this framework there can be two geometrical forms, either cis (6a) or trans (6b) as far as the Cp ligands are concerned, the situation is of course more complicated when $X \neq Y$.



6a



6b

As mentioned before, compounds of the type Cp_2ML_2 (where L = monodentate) are quite numerous and have well-known tetrahedral geometry, containing the angular Cp_2M moiety. However compounds of the type $Cp_2M(chelate)_2$ are very rare. A very recent structure by Marks *et al.*,[95] of $(\eta^5\text{-}MeC_5H_4)_2Hf(BH_4)_2$ has shown that the $(MeCp)_2Hf$ fragment retains the angular cisoid arrangement. As well, the preliminary X-ray analysis of the compound $Cp_2U(BH_4)_2$ [32] suggests a structure consisting of a tetrahedral arrangement of the Cp and BH_4 ligands around the uranium centre. In a succeeding chapter it will be shown that the instantaneous structure of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$

is also consistent with a cis octahedral structure.

Of course there exists a large number of compounds of the type M(chelate)$_2$XY both for main group and transition metals. Interestingly for group IV metals the cis configuration about the metal centre seems to be the preferred geometrical form. This has been shown for Sn(acac)$_2$X$_2$ (X = Cl, Br, I),[97,98] Sn(acac)$_2$RCl[99] and for a variety of Ti(chelate)$_2$XY compounds (chelate = dithiocarbamate,[84] acetylacetonate).[100,101] Based on these examples, in particular by analogy with the known Cp$_2$M(chelate)$_2$ complexes, it would be reasonable to state that the present compounds also possess the cis octahedral geometry 6a.

An attempt to corroborate this assignment was made by analyzing the NMR spectra of the bis(cyclopentadienyl) compounds. The ambient temperature results are summarized in Table X. As expected for compounds containing a paramagnetic metal ion, U(IV)(5f^2), the resonances exhibit large shifts from the expected diamagnetic positions.[58] The upfield shifts observed for the Cp rings in Cp$_2$U(O$_2$CNEt$_2$)$_2$ and Cp$_2$U(OSCNEt$_2$)$_2$ are in line with previous observations on cyclopentadienyl containing uranium compounds, but the downfield shift seen in Cp$_2$U(S$_2$CNEt$_2$)$_2$ is unusual.[13d] Since it is known that both dipolar and contact terms are important in determining the observed isotropic shifts, variations in either could account for the trend observed in the present series. The single sharp lines obtained

Table X. ^{1}H NMR Data for $Cp_2U(XYCNEt_2)_2$ Complexes[a]

	$Cp_2U(S_2CNEt_2)_2$	$Cp_2U(OSCNEt_2)_2$	$Cp_2U(O_2CNEt_2)_2$
Cp	-.44 s	2.84 s	7.73 s
CH_2	11.37 q	-5.28 q	8.07 q
		13.64 q	
CH_3	10.87 t	-.84 t	8.53 t
		11.82 t	

[a] ppm from internal benzene, + upfield shift, -downfield shift. Temp = 35°C.

for the Cp groups indicate equivalence of the attached hydrogen atoms, consistent with the assigned pentahapto bonding mode for these ligands. Equivalence of the ethyl groups may also be indicated by the observation of one set of quartet (CH_2) and triplet (CH_3) resonances in the symmetric CS_2 and CO_2 inserted compounds. The monothiocarbamate derivative exhibits two equal intensity ethyl resonances, although there is still only one cyclopentadienyl peak. The significance of a simple ^1H NMR spectrum obtained for $Cp_2U(O_2CNEt_2)_2$ is obscured by the probably fast intermolecular exchange between different polymeric aggregates. In what follows, the discussion will be restricted to the behavior of the dithio- and monothiocarbamate complexes whose monomeric nature in benzene has been established.

Clearly the ambient temperature ^1H NMR spectra are not consistent with the static structure 6a. For instance two ethyl resonances are expected for $Cp_2U(S_2CNEt_2)_2$. A number of possible reasons exist for these apparently simplified spectra. It is known that the chemical shifts of paramagnetic compounds are temperature dependent so that accidental chemical shift equivalence of some ligand resonances may be responsible for the observed spectra at room temperature. Another factor pertinent to these complexes is the fact that stereochemical nonrigidity is common among metal carbamates. Indeed it is well known that the NMR line shapes of metal carbamates are often affected by two main kinetic processes:[102] i) metal-centered rearrangement; ii) $C\overset{\cdots}{-}N$ bond rotation. The observation of metal centered rearrangement in related $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$[103] is further support for considering nonrigidity in the present case.

Four situations must be considered involving various combinations of metal-centered rearrangement and $C\overset{\cdots}{-}N$ bond rotation that can be either fast or slow on the NMR time scale. The predicted number of resonances for the Cp and R groups in $Cp_2U(XYCNR_2)_2$ are indicated in Table XI for the following cases: (A) metal-centered rearrangement and $C\overset{\cdots}{-}N$ bond rotation are both slow on the NMR time scale; (B) metal-centered rearrangement is slow, but $C\overset{\cdots}{-}N$ bond rotation is fast; (C) metal-centered rearrangement is fast, but $C\overset{\cdots}{-}N$ bond rotation is slow; and (D) both processes are fast. A few comments must be made concerning Table XI. A full permutational analysis of metal-centered rearrangement processes in $cis\text{-}M(AA)_2X_2$ and $cis\text{-}M(AB)_2X_2$ has been carried out by Serpone and Bickley.[104] These authors have considered the effects of the trigonal-twist about each of the four imaginary C_3 axes of 6a, as well as the possibility of metal-chelate bond cleavage and subsequent rearrangements of the so produced five-coordinate intermediate. Obviously the possibilities are numerous and the delineation of probable

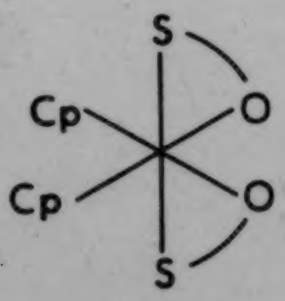
Table XI. Predicted Number of Resonances for the Cp- and R-Groups Respectively in $Cp_2U(XYCNR_2)_2$ for Various Rearrangement Possibilities.

	Symmetry	(A)	(B)	(C)	(D)
$Cp_2U(X_2CNR_2)_2$	C_2	1,2	1,1	1,1	1,1
$Cp_2U(OSCNR_2)_2$	C_2[a]	1,2	1,1	1,2	1,1
	C_2[a]	1,2	1,1		
	C_1[b]	2,4	2,2	2,2	2,1

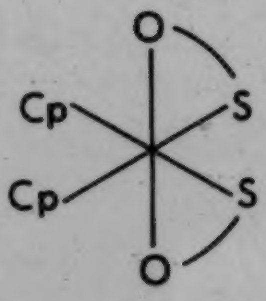
[a] Sulfur or oxygen of monothiocarbamate trans to each other.

[b] All cis compound.

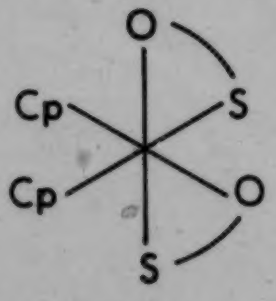
physical pathways for rearrangement in this class of molecules, as in others, requires carefully designed molecules undergoing specific line collapses. The present molecules do not satisfy these stringent requirements and in constructing the table only the chemically most reasonable rearrangement pathway has been taken into account. This pathway is that of a trigonal-twist motion which converts the starting octahedron to a prismatic intermediate, with the two chelating ligands situated along the rectangular edges, a Bailar-twist type motion. Keeping the foregoing discussion of the rearrangement in mind, the entries in Table XI for the symmetric $Cp_2U(X_2CNEt_2)_2$ cases become self-explanatory, however the many possibilities appearing against $Cp_2U(OSCNEt_2)_2$ may still require some comments. This molecule can actually exist as three distinct cis geometrical isomers once the location of the O and S donor functions are taken into account, 7a-c. Under static conditions isomers 7a and 7b



7a



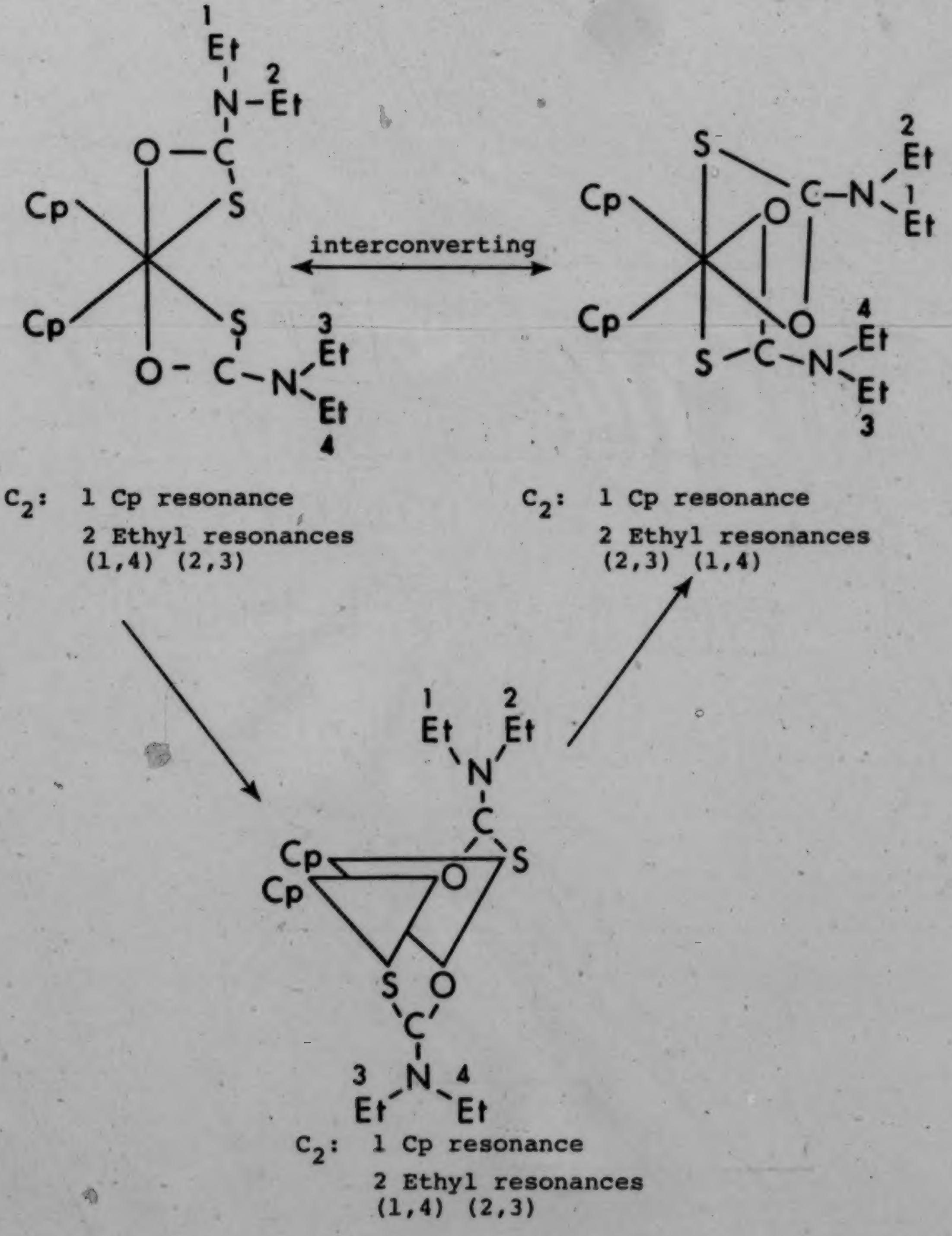
7b



7c

should each exhibit one Cp and two ethyl resonances. However a rapid Bailar-twist would interconvert the two isomers (Figure V), thus resulting in the observation of an averaged Cp and two sets of averaged ethyl resonances, entries 1, 2 under case (C). Of course C$\overset{\cdots}{-}$N bond rotation would further average the ethyl resonances to finally give one Cp and one ethyl signal, entries 1,1 under case (D). In a similar manner the entries for isomer 7c, symmetry C_1, can be obtained. In principle then, from $Cp_2U(OSCNEt_2)_2$ one could expect to see twelve sets of resonances, four Cp and eight ethyl group signals, under static conditions.

In order to distinguish between the possibilities listed above, the variable temperature NMR data were collected for the compounds $Cp_2U(OSCNEt_2)_2$ and $Cp_2U(S_2CNEt_2)_2$ in the solvent toluene. For the monothiocarbamate complex, cooling the sample down to -90°C caused broadening of the ethyl resonances, however the Cp resonance remained sharp. Warming the sample up to +92°C produced almost the same effect, a sharp Cp resonance and only slightly broadened ethyl resonances. The ^1H NMR spectrum of $Cp_2(OSCNEt_2)_2$ at 42°C is given in Figure VI. The ^1H NMR spectrum of $Cp_2U(S_2CNEt_2)_2$ at -60°C also showed a sharp Cp resonance and broad ethyl resonances. As the temperature was raised, the ethyl resonances sharpened, "coalesced" to a singlet at 90°C and separated again at higher temperature. That the "coalescence" was really a merging of peaks due


interconverting
Cp
Cp
Et
N
C
O
S
1
2
3
4

C$_2$: 1 Cp resonance
2 Ethyl resonances
(1,4) (2,3)

C$_2$: 1 Cp resonance
2 Ethyl resonances
(2,3) (1,4)

C$_2$: 1 Cp resonance
2 Ethyl resonances
(1,4) (2,3)

Figure V: Intramolecular Nonbond-Rupture Mechanism for Interconverting One Set of Isomers of $Cp_2U(OSCNEt_2)_2$.

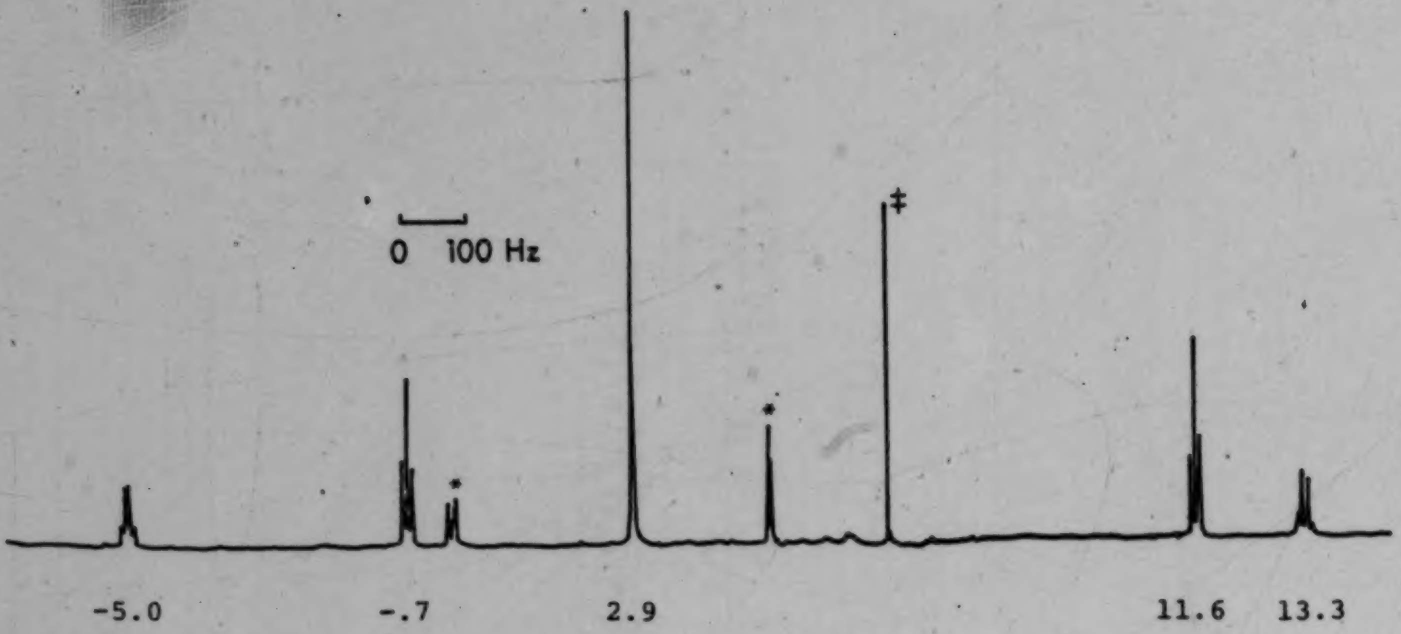


Figure VI: ^{1}H NMR Spectrum of $Cp_2U(OSCNEt_2)_2$ at 42°C.

*Solvent toluene.

‡grease.

chemical shift given in ppm relative to aromatic toluene.

to the different temperature dependence of the methylene and methyl chemical shifts can be seen in Figure VII or more clearly in Figure VIII which shows the variation of the chemical shifts as a function of temperature.[39] The linear behavior found is commonly observed with organouranium(IV) compounds. Figure IX shows this variation for $Cp_2U(OSCNEt_2)_2$. The temperature invariant nature of the line shapes was disappointing, however it is highly improbable that accidental chemical shift equivalence would account for the pattern of Cp and ethyl resonances observed. As mentioned previously, the presence of the paramagnetic U(IV) ion has the effect of amplifying the chemical shift differences between groups, this should diminish the chance of accidental equivalence compared to diamagnetic compounds. Furthermore, as can be seen in Figures VII, VIII and IX the chemical shifts in paramagnetic compounds are temperature dependent as well, thus the accidentally overlapping resonances would also have to have identical temperature dependent chemical shifts in order to maintain the simple spectrum at all temperatures. This situation for the complicated spectrum expected for $Cp_2U(OSCNEt_2)_2$ seems indeed virtually impossible.

If it is assumed that rearrangement processes are responsible for the observed NMR spectra, it is clear that in the case of $Cp_2U(S_2CNEt_2)_2$ several possibilities

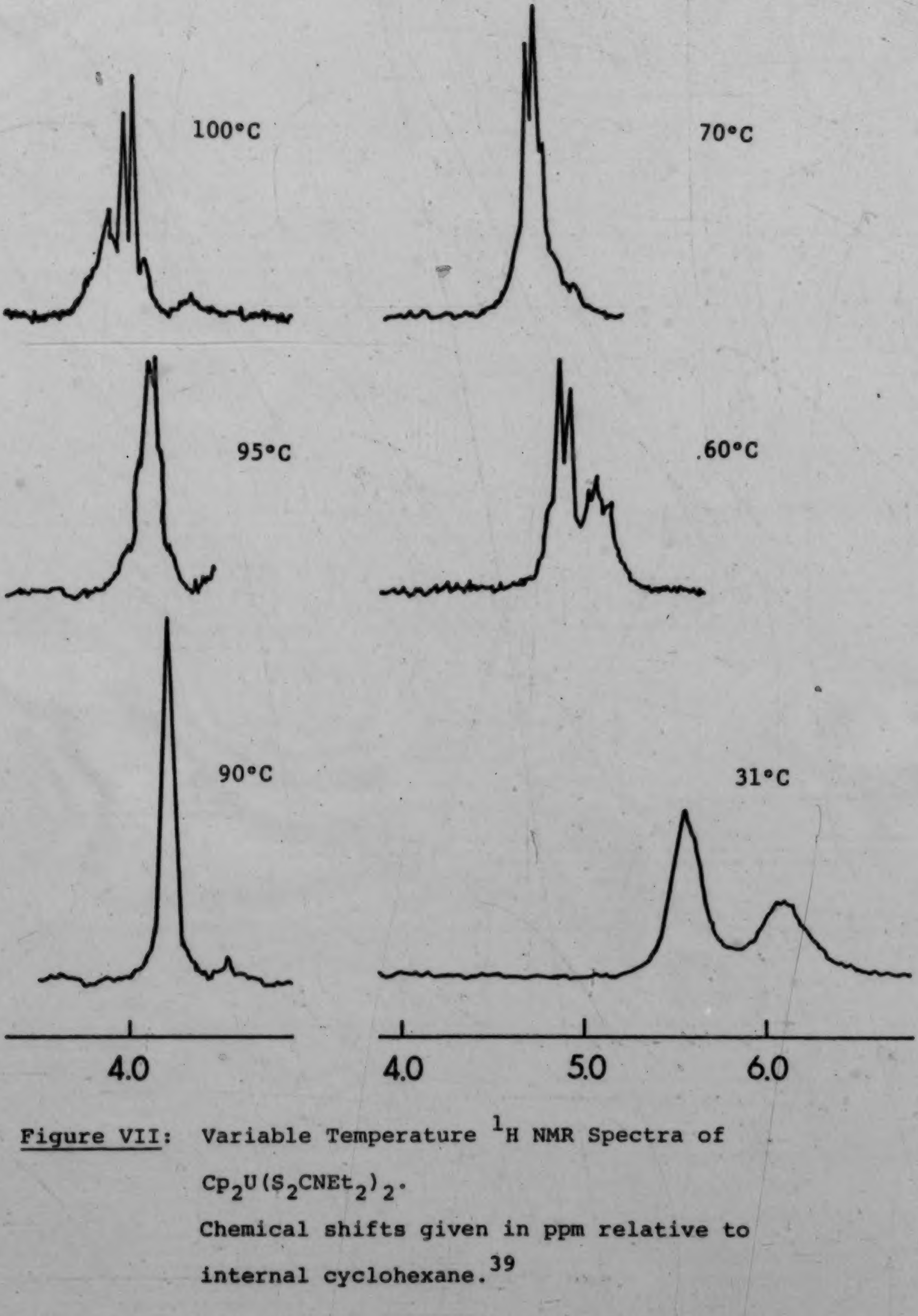


Figure VII: Variable Temperature ^1H NMR Spectra of $Cp_2U(S_2CNEt_2)_2$. Chemical shifts given in ppm relative to internal cyclohexane.[39]

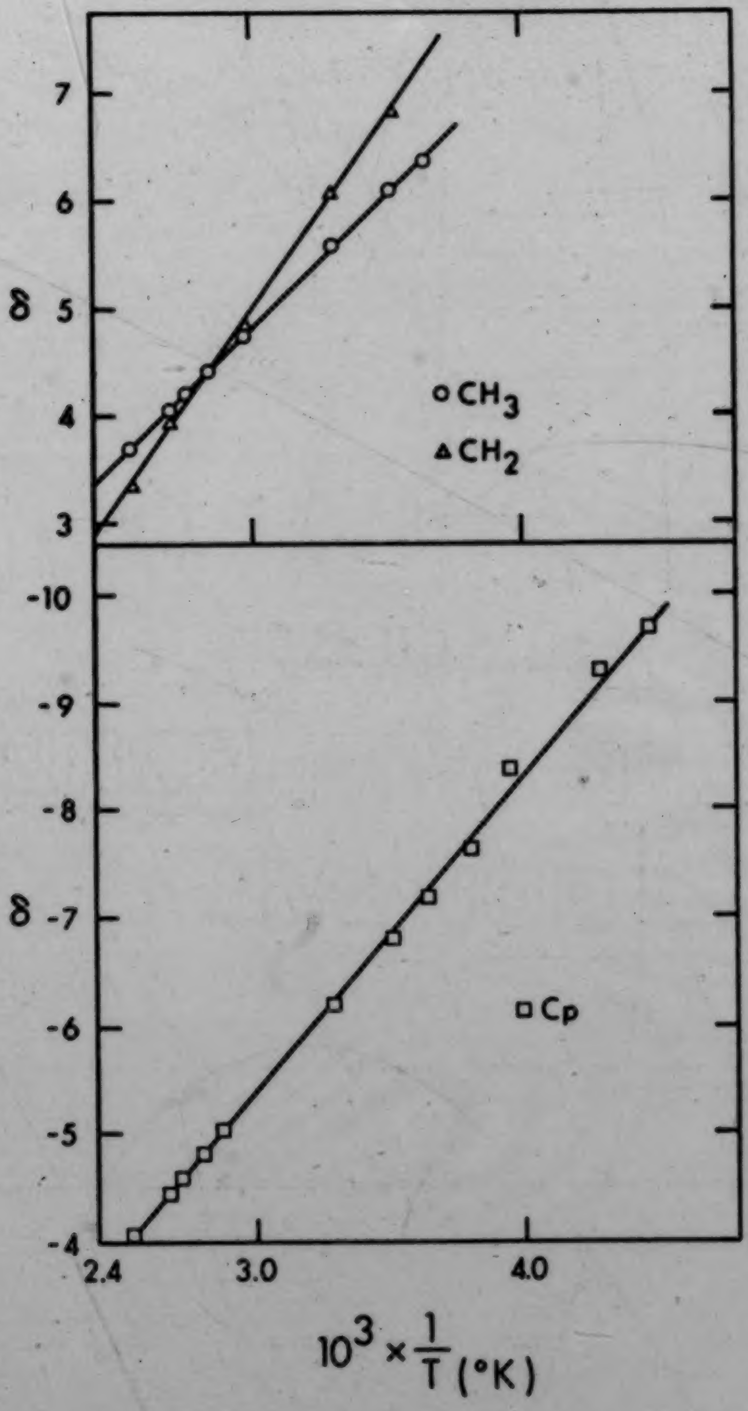


Figure VIII: Chemical Shift of Protons of $Cp_2U(S_2CNEt_2)_2$ versus 1/T.

Chemical shifts given in ppm relative to internal cyclohexane.[39]

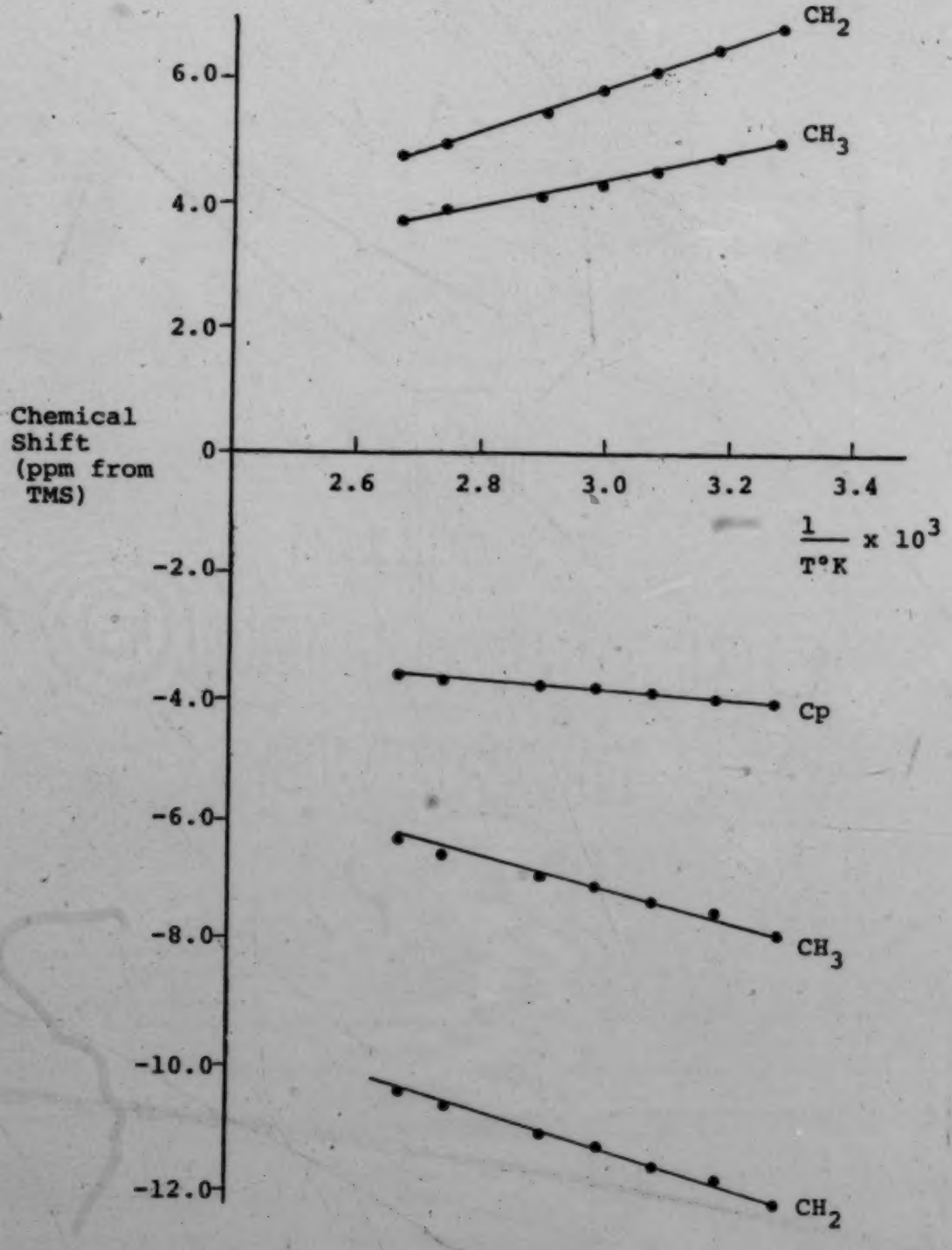


Figure IX: Chemical Shift of Protons of $Cp_2U(OSCNEt_2)_2$ versus 1/T.

could account for the experimental spectra. More discrimination is offered however by the monothiocarbamate complex. Indeed, any assumed mechanism must maintain two ethyl groups distinct during the rearrangement process. Reference to Table XI shows that an attractive possibility for this, as long as the ground state geometry is the symmetric structure 7a and/or 7b, is case (C) where rapid metal-centered rearrangement but slow $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond rotation is occurring. Precedent for fast metal-centered rearrangement down to the lowest accessible temperatures (-90°C) in similar complexes, cis-$Ti(S_2CNR_2)_2Cl_2$, has been obtained by Fay *et al.*[84] Whereas Chisholm[90b] and Bagnall[65] have reported that in $Ti(OSCNMe_2)_4$ and $Th(OSCNEt_2)_4$ $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond rotation is slow on the NMR time scale at 40 and 50°C, respectively. Comparison of the $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching frequency of the thorium complex, 1915 cm^{-1} with the almost identical values of $Cp_2U(OSCNEt_2)_2$ (Table IX) suggests that $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond rotation should also be slow in this complex. By analogy it is assumed that possibility (C) is operational in the dithiocarbamate complex as well. Although consistent with the NMR data obtained, the combination Bailar-twist and hindered $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ bond rotation requires the presence of only symmetric thiocarbamate complexes in solution. The presence of a sharp single Cp resonance would suggest that not all three isomers, 7a, b, c, are present at the same time, since it would be unlikely that the Cp resonances would all have the same chemical shifts over the temperature range studied. However, whether only 7a, b exists or only 7c, the asymmetric compound undergoing more complicated nonrigid behavior in solution, must await the result of X-ray structural work.

It should be noted that although the cis form, 6a, has been favoured in the discussion, the trans form, 6b, cannot be dismissed on the basis of the spectroscopic data presented to date. Again, structural results would be very useful.

Conclusions

The reagent $Cp_2U(NEt_2)_2$ has been shown to undergo insertion reactions with CS_2, COS and CO_2 to give carbamates of the type $Cp_2U(XYCNEt_2)_2$ (XYC = S_2C, OSC, O_2C). The molecular weight data showed that while $Cp_2U(S_2CNEt_2)_2$ and $Cp_2U(OSCNEt_2)_2$ were monomeric in benzene, $Cp_2U(O_2CNEt_2)_2$ gave indications of polymeric behavior. The spectroscopic data are consistent with a pseudo-octahedral geometry containing bidentate carbamate ligands and pentahapto cyclopentadienyl groups occupying mutually cis positions. However the exact isomeric form of the unsymmetrical compound, $Cp_2U(OSCNEt_2)_2$, existing in solution could not be determined. The variable temperature ^1H NMR spectra of the molecules were interpreted in terms of metal-centered rearrangement processes with restricted $C\overset{\cdots}{-}N$ bond rotation.

The properties of the present uranium complexes are not significantly different from those of certain transition metal carbamates in that a bidentate coordination mode and non-rigid behavior are observed. However comparison with the exactly analogous transition metal complexes is not possible since transition metal compounds containing two cyclopentadienyl and two carbamate ligands have not been prepared as yet. Indeed the interesting question to pose would be whether or not these transition metal complexes would retain the bidentate coordination mode of the carbamate moiety or exhibit monodentate behavior.

CHAPTER FOUR

CARBOXYLATE DERIVATIVES OF BIS(CYCLOPENTADIENYL)URANIUM(IV)

Introduction

Carboxylic acids have been used quite extensively as ligands with a wide variety of metals.[105,106] The prevalence of the carboxylate ligand system, RCX_2^-, is a result of the variations available in both the choice of R and X moieties (commonly S or O) and the ligating mode (monodentate, bidentate or bridging). Carboxylate derivatives of uranium(IV) have been known for some time since this flexible ligand allows the uranium centre to attain high coordination numbers and thereby form quite stable compounds. Some of the earliest complexes prepared have been of the type $U(O_2CR)_4$, which were reported in 1932 for the formate and acetate ligand systems.[107] The synthetic and structural aspects of carboxylate derivatives of both lanthanides and actinides have been reviewed up to 1972 by Bagnall.[108] In Table XII is listed a number of the more common uranium(IV) carboxylates produced to date.

The tetrakiscarboxylates are stable at room temperature although they are slowly oxidized by air to uranyl (VI) species. For this reason the compounds are normally handled under an inert atmosphere. Although these compounds have generally been well characterized by elemental

Table XII. Tetrakiscarboxylates of Uranium(IV)

Compound	Reference
$U[O_2CMe]_4$	109,110
$U[O_2CEt]_4$	109,110
$U[O_2CCHMe_2]_4$	109,110
$U[O_2CCH_2CHMe_2]_4$	110,111
$U[O_2C(CH_2)_4Me]_4$	109
$U[O_2CPh]_4$	109
$U[O_2C(CH_2)_5Me]_4$	110
$U[O_2CCF_3]_4$	110
$U[O_2CCH_2Cl]_4$	111
$U[O_2CCCl_3]_4$	111
$U[O_2CCF_3]_4$	111
$U[O_2CCMe_3]_4$	111
$U[O_2C(CH_2)_3Me]_4$	111
$U[O_2CCHCl_2]_4$	111
$U[O_2CMe]_2[O_2CSC_4H_3]_2$	112

analyses and visible and infrared spectroscopy, very little NMR data have been reported.

Among the few structural studies carried out to date is the X-ray analysis of $U(O_2CMe)_4$. The uranium centre is ten coordinate in a polymeric array with both bridging and bidentate acetate groups.[113] Polymeric behavior has also been postulated for some of the non-halogenated carboxylates (R = $Me(CH_2)_2CH_2$, Me_2CHCH_2 and Me_3C)[111] based on their low solubility in common organic solvents. Judging from the stability of the tetrakis-carboxylates, it was hoped that bis(cyclopentadienyl)-uranium(IV) carboxylates would be more stable than $Cp_2U(NEt_2)_2$ and other $Cp_2U(NR_2)_2$ compounds because of the increased steric bulk and chelation effects of the carboxylate group. It was anticipated that the reagent, $Cp_2U(NEt_2)_2$, would react with the acidic hydrogen in an acid displacement reaction, as shown in equation (IV-1).

$$Cp_2U(NEt_2)_2 + 2RCXYH \longrightarrow Cp_2U(XYCR)_2 + 2HNEt_2 \qquad \text{(IV-1)}$$

There are no reported organouranium(IV) compounds containing the cyclopentadienyl group as well as the carboxylato moiety, however among the transition metals there are a number of such complexes known. In general, only selected compounds contain chelating or bridging carboxylate groups. It is found that the monocyclopentadienyl derivatives of the early transition metals contain bidentate carboxylate groups, chelating coordination in $CpZr(O_2CMe)_3$[114] and bridging coordination in $CpV(O_2CMe)_2$[115] and $[CpV(O_2CCF_3)_2]_2$.[116] Although when the transition metal complex contains two cyclopentadienyl rings then almost invariably, especially for $Cp_2M(O_2CR)_2$ type compounds, the carboxylate group is monodentate. This situation has been determined for such compounds as $Cp_2M(O_2CR)_2$ where M = Mo or W, R = CF_3, Ph,[117] $Cp_2Zr(O_2CCF_3)_2$,[115] $Cp_2Ti(O_2CPh)_2$[118] and a series of fluorinated carboxylate compounds $Cp_2Ti(O_2CR_f)_2$ (R_f = CF_3, C_3F_7, C_2F_5) and $Cp_2Zr(O_2CR_f)_2$ (R_f = CF_3, C_3F_7, $CF_3CF_2CF_2$).[119] Very recently there has appeared work by Pasynskii *et al.* on the synthesis of $Cp_2Nb(O_2CCF_3)_2$ and $Cp_2Nb(O_2CCMe_3)$.[120] Infrared and NMR spectroscopic data indicate monodentate carboxylate moieties in these complexes also.

The seldom observed occurrence of coordination number greater than eight in transition metal compounds might be offered as a rationale for the monodentate carboxylate ligands in the last class of $Cp_2M(O_2CR)_2$ complexes. The coordination number of the metal would formally be ten in all the compounds should they possess two bidentate carboxylate groups and counting the cyclopentadienyl ring as occupying three coordination positions.

Clearly it would be of interest to study the uranium system. The ubiquitous property of the actinide metals to exhibit high coordination numbers, commonly nine and ten, could in fact favour the presence of two bidentate carboxylates in $Cp_2U(XYCR)_2$ type compounds. In addition, it would also be instructive to study the effect of the R groups on possible aggregate formation as well as the changes in chemical and physical properties upon replacing the oxygen donor function with a sulfur atom.

Results and Discussion

Synthetic Aspects

The carboxylate and monothiocarboxylate derivatives of bis(cyclopentadienyl)uranium were formed easily in hydrocarbon solvents by the reaction of $Cp_2U(NEt_2)_2$ and two equivalents of the appropriate acid as outlined in equation (IV-2).

$$Cp_2U(NEt_2)_2 + 2RCOXH \xrightarrow[solv]{T} Cp_2U(OXCR)_2 \qquad (IV-2)$$

R = Me; X = O; S; T = 0°C; solv = hexane

R = Ph; X = O; T = 0°C; solv = toluene

R = Ph; X = S; T = 0°C; solv = hexane

R = CMe_3; X = O; T = 0°C; solv = hexane

The compounds were characterized by infrared and, where soluble, NMR spectroscopy and mass spectrometry.

a) $Cp_2U(O_2CMe)_2$

The pale green compound is insoluble in most organic solvents, but is soluble in pyridine. However an NMR sample prepared in pyridine-d_5 only showed cyclopentadiene (C_5H_6) peaks indicating that hydrolysis had occured.

An attempt to crystallize some product by adding hexane to a pyridine solution resulted in the formation of only a very small amount of a fine green precipitate. All the solvents were removed under vacuum and a gold-brown solid was obtained, which was also insoluble in deuteriobenzene. The mass spectrum of this gold-brown solid indicated that the most volatile component was now $CpU(O_2CMe)_3$. Water in the pyridine may have caused hydrolysis and subsequent rearrangement to the mono-(cyclopentadienyl) compound however the fact that peaks corresponding to this compound or any other uranium-containing species were not seen may be due to the choice of sweep width. The region searched was from 20 ppm below internal pyridine to 60 ppm above. It is possible that the resonances are outside of this area.

b) $Cp_2U(OSCMe)_2$

This green solid was easily formed and is soluble in most organic solvents. No attempts were made to crystallize this compound. The compound was also soluble in pyridine, however as seen before for $Cp_2U(O_2CMe)_2$ an NMR sample in pyridine-d_5 showed only cyclopentadiene peaks in the region 0-20 ppm from internal pyridine.

c) $Cp_2U(OSCPh)_2$

This red compound was soluble in most organic solvents. Several crystallization attempts were made using mixtures of either toluene/hexane or CH_2Cl_2/hexane at room temperature, 0°C and -78°C, but either a very fine precipitate or a red oil formed. Attempts at cooling supersaturated solutions of either toluene or CH_2Cl_2 also failed to produce crystals.

d) $Cp_2U(O_2CPh)_2$

This pale green solid is slightly soluble in THF however attempts to crystallize the compound using a cooled THF/hexane solvent mixture were met with failure.

The mass spectrum of the green solid contained almost exclusively $Cp_2U(O_2CPh)_2$ whereas a mass spectrum obtained from a sample of green solid exposed to air had a fragmentation pattern assignable to $Cp_3U(O_2CPh)$. Excess acid, PhCOOH, was added to the brown filtrate solution from the original preparation in order to react with any remaining starting material. Mass spectral analysis of the brown precipitate which was formed indicated the presence of a mixture of mainly $CpU(O_2CPh)_3$, some $Cp_2U(O_2CPh)_2$ and a little $U(O_2CPh)_4$. Clearly maintaining the stoichiometry of the reaction is important since the cyclopentadienyl group can undergo ready displacement by excess acid. The compound $Cp_2U(O_2CPh)_2$ dissolved in pyridine, however cyclopentadiene peaks were observed indicating hydrolysis. Other peaks were also seen, shifted considerably from those positions normally observed for Cp_2U derivatives (i.e., singlet at -77 ppm from pyridine). These peaks could not be assigned, although judging from the splitting patterns it was apparent that they were caused by phenyl-containing species.

e) $Cp_2U(O_2CCMe_3)_2$

This compound was the only one of the carboxylates which could be crystallized. Cooling a concentrated hexane solution resulted in the formation of green crystals.

f) $Cp_2U(NEt_2)(O_2CCMe_3)$

An attempt to produce only the mono-substituted carboxylate compound resulted in a mixture of both the mono- and bis-substituted complexes according to equation (IV-3):

$$3Cp_2U(NEt_2)_2 + 3Me_3CCOOH \xrightarrow[\text{hexane}]{\text{r.t.}} \qquad \text{(IV-3)}$$

$$Cp_2U(O_2CCMe_3)_2 + Cp_2U(NEt_2)(OCCMe_3) + Cp_2U(NEt_2)_2$$

It was thought that a possible equilibrium may be occurring, however cooling an NMR sample resulted in a shifting of peak positions but the relative intensity of the peaks remained the same.

Attempts to fractionally crystallize out the mono-substituted product by concentrating the solution and cooling failed to produce any solid material.

Molecular Weight Determination

Molecular weight data could be obtained for only two compounds. $Cp_2U(OSCPh)_2$, was shown to be a monomer, whereas $Cp_2U(O_2CCMe_3)_2$ exhibited dimeric behavior. Determinations were not performed on $Cp_2U(OSCMe)_2$ or $Cp_2U(O_2CMe)_2$ due to thermal decomposition of the former and insolubility of the latter. It can be inferred from the solubility properties of $Cp_2U(O_2CMe)_2$ and $Cp_2U(O_2CPh)_2$

that these compounds are polymers, since the dimeric $Cp_2U(O_2CCMe_3)_2$ is soluble in hexane whereas the first two compounds are insoluble in hydrocarbon solvents.

This assessment of the structural configuration will be discussed later in terms of the infrared parameters of the compounds.

Mass Spectral Data

The mass spectral data for major fragmentation patterns for the $Cp_2U(IV)$ carboxylates are summarized in Table XIII and Table XIV. The compounds are volatized at a relatively low temperature and in fact for $Cp_2U(OSCMe)_2$ and $Cp_2U(O_2CCMe_3)_2$ sublimation occurs at a temperature of 100°C under a vacuum of .025 mm Hg. The strong relative abundance of the molecular ion peak observed for all the compounds attests to their robust nature. It is striking that the monothiocarboxylate derivatives possess larger parent ion peaks than the corresponding carboxylate complexes; for $Cp_2U(OCSMe)_2$ the relative abundance is approximately 1.5 times as much as for the compound $Cp_2U(O_2CMe)_2$. This same trend was noticed for the insertion compounds, $Cp_2U(XYCNEt_2)_2$, where the relative abundance of $Cp_2U(OSCNEt_2)_2$ is slightly greater than that of $Cp_2U(O_2CNEt_2)_2$

The base peak for this series of compounds, as for almost all other Cp_2U derivatives, results from loss of

Table XIII: Summary of Mass Spectral Data for $Cp_2U(carboxylate)_2$[a] Complexes.

	$Cp_2U(O_2CPh)_2$			$Cp_2U(OSCPh)_2$		$Cp_2U(OSCMe)_2$		$Cp_2U(O_2CMe)_2$		$Cp_2U(O_2CCMe_3)_2$	
	m/e	rel. abund[b]	rel. abund[c]	m/e	rel. abund[d]	m/e	rel. abund[e]	m/e	rel. abund[f]	m/e	rel. abund[g]
P^+	610	24.5	21.0	642	28.6	518	39.6	486	25.3	570	19.7
$P-Cp^+$	545	100	100	577	100	453	100	421	100	505	100
$P-(XYCR)^+$	489	12.8	14.3	505	1.4	443	4.6	427	5.9	469	15.7
$P-Cp-(XYCR)^+$	424	1.1	.7	440	1.0	378	1.0	362	.6	404	.9
$[P-Cp-(XYCR)]SH^+$	-	-	-	473	.5	411	12.3	-	-	-	-
$[P-Cp-(XYCR)]OH^+$	441	2.3	.6	457	1.2	395	22.7	379	40.0	421	4.3
$[P-Cp-(XYCR)]S^+$	-	-	-	472	1.8	410	.6	-	-	-	-
$[P-Cp-(XYCR)]O^+$	440	4.9	3.6	456	6.8	394	2.2	378	3.3	420	2.3
$CpU(XYCR)(R)^+$	501	.8	.7	517	.9	393	.3	377	.2	461	0.0
Cp_2UO^+	384	3.5	1.8	384	.8	384	.8	384	2.6	384	3.2
$CpUO^+$	319	23.4	16.2	319	21.8	319	39.7	319	27.7	319	12.3
UOS^+	286	-	-	286	4.1	286	12.9	-	-	-	-
UO_2^+	270	21.3	11.8	270	16.3	270	12.3	270	22.0	270	5.7
US_2^+	302	-	-	302	.9	302	1.7	-	-	-	-
Peaks higher than P^+		No	No	No		No		Yes		Yes (high temp only)	

Footnotes for Table XIII

[a] Not corrected for ^{13}C, rel. abundance given in %

[b] T = 130°C

[c] T = 150°C

[d] T = 125°C

[e] T = 120°C

[f] T = 120°C-150°C

[g] T = 100°C

Table XIV: Major Fragmentation Processes for $Cp_2U(carboxylate)_2$ Complexes

	Metastable Peaks									
	$Cp_2U(O_2CPh)_2$		$Cp_2U(OSCPh)_2$		$Cp_2U(O_2CMe)_2$		$Cp_2U(OSCMe)_2$		$Cp_2U(O_2CCMe_3)_2$	
Process	calc'd	found	calc'd	found	calc'd	found	calc'd	found	calc'd	found
$P^+ \longrightarrow P\text{-}Cp^+ + Cp$	486.9	487.0	518.6	519.0	364.7	365.0	396.2	396.0	447.4	447.5
$P^+ \longrightarrow [P\text{-}XYCR]^+ + XYCR$	392.0	392.0	397.2	not seen	375.2	375.0	278.9	not seen	385.9	386.0
$P\text{-}Cp^+ \longrightarrow [P\text{-}Cp\text{-}XYCR]O^+ + XCR$	355.2	355.3	360.4	360.5						
$\longrightarrow [P\text{-}Cp\text{-}XYCR]OH^+ + XCR\text{-}H$					341.2	341.5	344.4	344.5	351.0	351.0
$\longrightarrow [P\text{-}Cp\text{-}XYCR]SH^+ + YCR\text{-}H$							372.9	373.0		

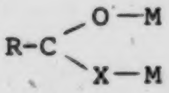
the cyclopentadienyl ligand from the parent ion. Loss of the carboxylate ligand is less likely to occur although it is one of the major fragmentation processes. A comparison of the relative abundance of the fragment ions arising for this process also shows that the carboxylate ligand is more labile than the monothiocarboxylate moiety, 12.8% for $Cp_2U(O_2CPh)_2$ as opposed to only 1.4% for $Cp_2U(OSCPh)_2$.

Peaks above the molecular ion are observed for $Cp_2U(O_2CMe)_2$, and $Cp_2U(O_2CCMe_3)_2$. Although molecular weight determination for the pivalate derivative indicated dimer formation, this ion was not observed. In fact the high mass peaks, for $Cp_2U(O_2CCMe_3)_2$, were only seen at higher temperatures (> 150°C) and then only breakdowns involving loss of cyclopentadienyl and pivalate ligands were observed. The existence of high mass peaks in the spectrum of $Cp_2U(O_2CMe)_2$ is not unexpected since based on its insolubility it is assumed that the molecule is associated in the solid state and that this could persist in the gas phase as well. The fact that the tetrakisacetate complex is a polymer might also support the above postulate.[113] As in the case of the pivalate compound, no ion corresponding to a dimer or trimer was seen in the acetate spectrum, although peaks corresponding to losses of cyclopentadienyl and acetate from these units were observed. Other high field peaks did not seem to correspond to chemically reasonable clusters and it has been proposed that some high mass peaks can result from recombinations within the spectrometer caused by the direct insertion method and the high ionizing energy used.[106,121]

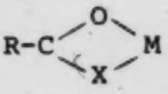
Loss of the CX_2 moiety was very minimal as opposed to the mass spectral behavior of the insertion compounds discussed in Chapter III. Rearrangement of molecular fragments to uranium-carbon bonded species is apparently not favoured.

Infrared Spectral Data

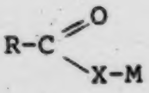
The structural role assumed by polydentate ligands can usually be clarified by the use of infrared spectra. The carboxylate ligand system can coordinate to the metal as a monodentate, bidentate or bridging moiety. More flexibility results when a monothiocarboxylate group is involved because of the different coordinating ability of the sulphur and oxygen atoms towards a metal centre. A wide variety of bonding mode options are available as the following diagrams show:



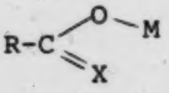
8a



8b



8c



8d

X=S or O

It is apparent from the diagrams that as the coordination mode changes from monodentate to bidentate (chelating or bridging) there is a decrease in the double bond character of the C=O or C=S bond. In addition in the case of the carboxylate function, the symmetry of the ligand also increases from C_s to C_{2v}. In principle, infrared spectroscopy should be able to monitor both of these effects. Correlations have been made between the band position in the infrared and bonding mode for carboxylate[106] and monothiocarboxylate groups. The carboxylate ion exhibits two bands due to the symmetric and asymmetric C-O stretching modes. When the carboxyl group is monodentate, one of the C-O bonds will have increased double bond character and give rise to a high frequency band. This behavior can be observed among the main group metals. For instance the compounds $H_3M[OC(O)\text{-}Me]$, M = Si and Ge, are considered to have monodentate acetate groups since they exhibit high ν(C=O) stretches at 1750 cm^{-1} and 1730 cm^{-1} respectively.[122] Certain transition metal complexes like the $Cp_2Ti(O_2CR)$ compounds,[123] which would be expected to have bidentate ligands exhibit asymmetric and symmetric C-O stretches at lower frequencies, 1500-1550 cm^{-1} and 1425-1460 cm^{-1} respectively. The asymmetric stretch is normally easily assigned, however the symmetric stretch may be masked by other absorptions especially in a complex containing a cyclopentadienyl group since the ν(C-C) mode of the Cp ligand also absorbs between 1410-1440 cm^{-1} [13b] making precise assignments in this region difficult.

As well as monitoring the positions of the carbonyl stretching frequencies, the difference between the asymmetric and symmetric stretching frequencies, $\Delta\nu$, can also be used as a guide to the ligation of the carboxylate group.[105,106] It was noted that this number was approximately 100 cm^{-1} or less if there was a strong possibility of bidentate coordination, between 100 cm^{-1} and 200 cm^{-1} then bridging coordination was likely and greater than 200 cm^{-1} for monodentate coordination. It is easy to see the rationale behind these variations, at least for the two extreme bonding modes. For a monodentate carboxylate moiety the two C-O bonds become nonequivalent. The asymmetric vibration takes on more ketonic character and increases in frequency whereas the value for the symmetric mode decreases. Thus a large splitting of the $\nu(CO)$ frequencies is anticipated. For a bidentate bonding mode the C-O bonds are of similar nature and a decrease in the splitting of the two stretching frequencies should follow. This method, for instance, has been utilized in a series of titanium complexes containing both the cyclopentadienyl and carboxylate moieties to predict the bonding mode of the latter ligands. In the compounds $Cp_2Ti(O_2CR)$[123] a chelating carboxylate group was assigned based on $\Delta\nu$ values which were below 115 cm^{-1}. The corresponding value for the complexes

$CpTi(O_2CR)_2$[124] was 168 ± 3 cm^{-1} and suggested to the authors the presence of bridging carboxylate ligands. This assumption was further supported by the dimeric nature of the complex, as shown by molecular weight measurements, by the virtually diamagnetic behavior of the complexes and proven conclusively by the X-ray structural determination of the benzoate derivative, $CpTi(O_2CPh)_2$.[125] Finally for the complexes $Cp_2Ti(O_2CR)_2$ the large value of $\Delta\nu \simeq 300$ cm^{-1} was assumed to indicate monodentate carboxylate bonding mode.[118]

However there are some problems associated with the $\Delta\nu$ criterion. First, there is some overlap in the ranges associated with the different bonding modes. Catterick and Thornton[106] in their review show a range of 80 to 250 cm^{-1} for the bridging configuration. Robinson and Uttley[126], studying a series of Ru, Os, Rh, and Ir derivatives containing triphenylphosphine and carboxylate moieties, found that both the asymmetric and symmetric carboxylate band positions varied extensively. Meaningful interpretation of their data followed only if both the position of the asymmetric stretch and the differences in the carboxylate stretches were monitored. It thus appears that although the monodentate bonding mode is usually indicated by a combination of high frequency of the asymmetric C-O stretch and large splitting between the two ν(CO) modes, the prediction of bidentate or bridging chelation based on infrared considerations alone is not as conclusive.

A further complication that can arise is change in the ligating mode of the carboxylate group upon varying the phase. The compounds $Me_3Sn(OCOR)$ are monomeric with monodentate OCOR groups in solution ($\Delta\nu$ = 430 cm^{-1}, 406 cm^{-1}, 330 cm^{-1} for R = CF_3, CCl_3, Me) whereas they are polymers with bridging OCO groups in the solid phase ($\Delta\nu$ = 140 cm^{-1} for R = Me).[127]

Almost all of the uranium tetrakiscarboxylate compounds reported to date contain at least bidentate ligands, a result which is not surprising considering that a tendency towards higher coordination numbers is prevalent in uranium chemistry as well as a predisposition towards oxygen bonding. The differences between the asymmetric and symmetric stretching modes are less than 200 cm^{-1} but tend to be greater than 100 cm^{-1}. The compound $U(O_2CMe)_4$, known to be a polymer with bridging and chelating moieties,[113] has $\Delta\nu$ values of 160 and 170 cm^{-1}. A list of other uranium(IV) carboxylates are given in Table XV. The $\Delta\nu$ values are indicative of bidentate coordination although as mentioned previously the exact extent of aggregate formation and concurrent occurrence of bridging ligands cannot be assessed from this data alone.

Table XV: Infrared Frequencies of Carbonyl Bands of Uranium Carboxylates in cm^{-1}.

	ν_{asy}^{CO}	ν_{sym}^{CO}	$\Delta\nu$	ref.
$U(O_2CMe)_4$	1560m, 1515m	1400m, 1345s	160, 170	110
$U(O_2CEt)_4$	1570s, 1510s	1410s	160, 100	110
$U(O_2C(CH_2)_5Me)_4$	1520s	1410s	110	110
$U(O_2C(CH_2)_2Me)_4$	1520s	1440s	80	110
$U(O_2CCH_2Cl)_4$	1566vs	1426s	140	111
$U(O_2CCHCl_2)_4$	1590vs	1416s	174	111
$U(O_2CCl_3)_4$	1610vs	1425s	185	111
$U(O_2CCF_3)_4$	1625vs	1488s	137	111
$U(O_2CMe)_2(O_2CSC_4H_3)$	1540	1440, 1400	100, 140	112

The infrared spectroscopic data for the $Cp_2U(IV)$ carboxylates in the 1600-450 cm^{-1} region are listed in Table XVI. In Figure X and Figure XI are shown the infrared spectra of the carboxylate and monothiocarboxylate compounds.

The assignment of some of the bands in the spectra of the $Cp_2U(carboxylate)_2$ complexes is difficult because of overlap between vibrations arising from the cyclopentadienyl ring, the alkyl or aryl groups and the carboxylate functions.

The infrared pattern of the cyclopentadienyl ring in the present complexes consist of strong bands at around 1020 and 800 cm^{-1} assigned to the in-plane and out-of-plane C-H bending modes. Another vibration associated with the C-C stretching of the cyclopentadienyl ring at 1410-1450 cm^{-1} is obscured by the strong asymmetric C-O stretch of the carboxylate ligand also occurring in this area (*vide infra*). The simplicity of the pattern is indicative of a pentahapto bonding mode for the cyclopentadienyl moieties.[61]

The asymmetric and symmetric stretching modes for the alkyl carboxylates have been assigned to the strong bands which occur in the regions normally associated with these vibrations. As mentioned before the symmetric C-O stretching mode is in the same region as the ν(C-C) of the Cp ring and could have some contribution from the

Table XVI: Characteristic Infrared Absorptions of Cp$_2$U(carboxylate)$_2$ Complexes[a]

Assignment	Cp$_2$U(OSCPh)$_2$	Cp$_2$U(O$_2$CPh)$_2$	Cp$_2$(OSCMe)$_2$	Cp$_2$U(O$_2$CMe)$_2$	Cp$_2$U(O$_2$CCMe$_3$)$_2$
ν(C-C)phenyl	1596 m	1602 m			
		1591 m			
ν_{asym}(CO) -- $\nu(C\overset{\cdots}{-}O)$	1465 s	1494 s	1487 s	1523 s, vbr	1564 vs br
		1488 s			1484 s
ν_{sym}(CO)		1423 s		1463 s br	
				1416 s br	1424 s
	1226 vs	1179 m	1157 vs		1223 s
δ(C-H)Cp	1016 m	1022 s	1016 s	1016 s	1017 s
$\nu(C\overset{\cdots}{-}S)$	963 s		974 m		
γ(C-H)Cp	797 s	785 s	797 vs	789 s	786 s
$\Delta(\nu_{asym}-\nu_{sym})$		65, 71		60, 107	60, 140

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[a] In Nujol and Fluorolube mulls, given in cm^{-1}.

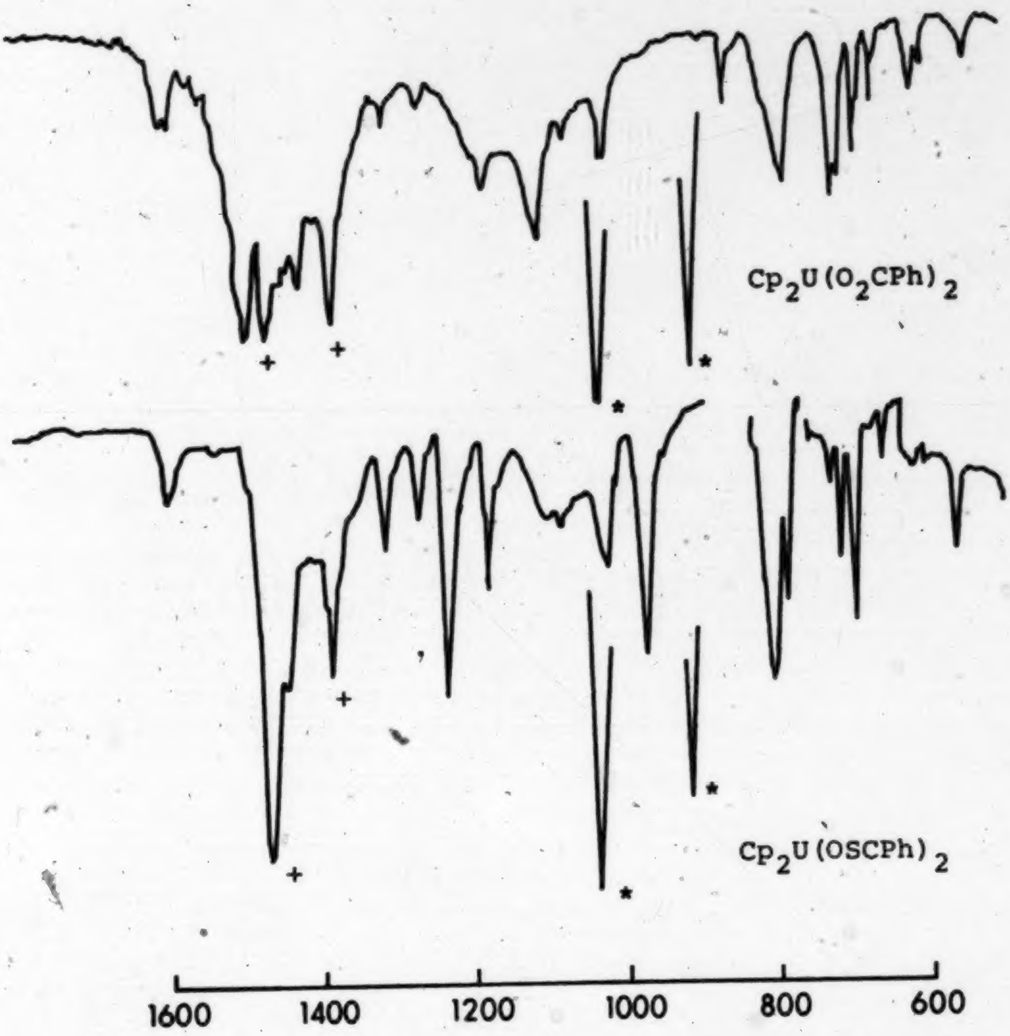


Figure X: Infrared Spectra of $Cp_2U(O_2CPh)_2$ and $Cp_2U(OSCPh)_2$.

*polystyrene.

+Nujol.

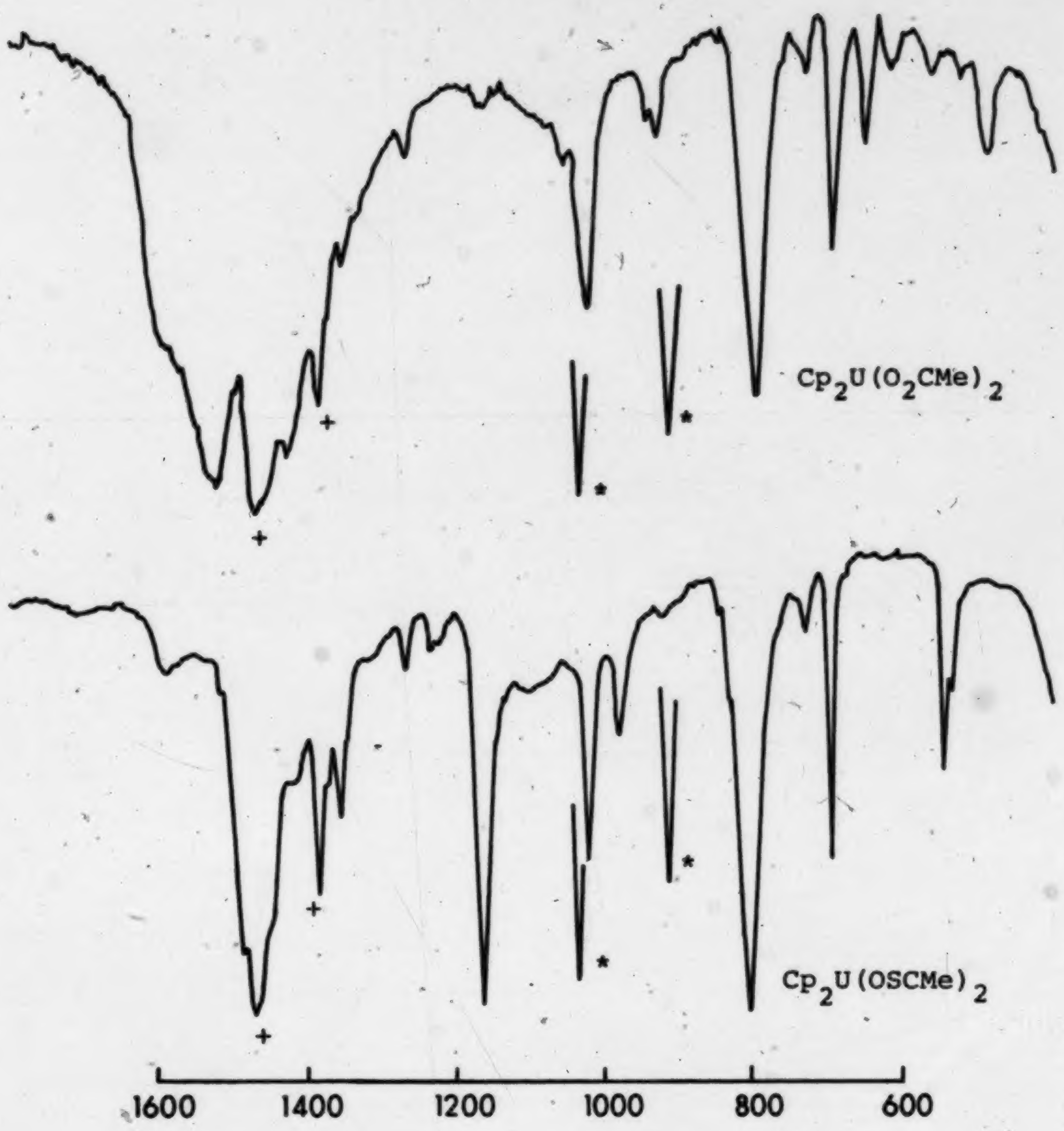


Figure XI: Infrared Spectra of $Cp_2U(O_2CMe)_2$ and $Cp_2U(OSCMe)_2$

*polystyrene

+Nujol

latter. In the case of the acetate, $Cp_2U(O_2CMe)_2$, and to a lesser extent the pivalate compound, $Cp_2U(O_2CCMe_3)_2$, these bands are quite broad. The cause of this broadness is not apparent unless it is related to the associated nature of the complexes. Unfortunately the ambiguity in assigning a definite band position tends to distract somewhat from the meaning of the $\Delta\nu$s listed in the table.

The spectrum of the benzoate complex poses a different problem. The strong bands at 1494 and 1488 cm^{-1} are probably due to the asymmetric C-O stretch, the low value for this frequency is not totally unexpected since the corresponding vibration in $Cp_2Ti(O_2CR)$ is found at 1505 cm^{-1}.[123] Although, as pointed out before, such a low frequency was taken as indicating a chelating carboxylate moiety; for $Cp_2U(O_2CPh)_2$ this value may denote instead carboxylate bridges, a result more consistent with the insoluble nature of the uranium complex. The benzoate complex also possesses two medium intensity bands at 1602 and 1591 cm^{-1}, which have been assigned to a phenyl vibration. In support of this assignment is the fact that mono-substituted benzenes usually absorb[128] in this region. As well a similar medium intensity band in the spectrum of $Cp_2U(OSCPh)_2$ is observed at 1596 cm^{-1} and a band at 1602 cm^{-1} has also been assigned to such a phenyl vibration in the $CpTi(O_2CPh)_2$[124] complex. Although it is possible that one of the two bands of $Cp_2U(O_2CPh)_2$

is due to a phenyl vibration and the other to a high frequency asymmetric C-O stretch, the almost invariably high intensity found for the latter vibration seems to mitigate against such an assignment. Thus it is argued that the $\Delta\nu$ values given in the table are indicative of chelating and/or bridging coordination mode for the carboxylate groups. The presence of bridging carboxylates would of course be consistent with the low solubility of the complexes which also suggest polymeric behavior. Unfortunately more precise structural inferences based on the infrared data cannot be made and structural work on some of these complexes would be very worthwhile to establish the extent of aggregate formation and details of the bonding modes of the carboxylate moieties.

The assignment of the bands for the monothiocarboxylate complexes was based on work by Nyquist *et al.* on thiol esters and related compounds,[129] by Patal *et al.*[130] on metal derivatives of thiobenzoate and by Coutts and Wailes[131] on $Cp_2Ti(OSCR)$ type compounds. The position of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ stretch and the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$ stretch would indicate that bidentate coordination has occurred. The low carbonyl frequency as mentioned before is indicative of this bonding mode.

The variety of bonding modes available for the monothiocarboxylate ligand have been diagramed before, figures 8a-d. The position of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ and $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$

bands have been used by Patal *et al.*[130] to determine which of these coordination modes are present in a series of transition-metal thiobenzoate complexes. Variation in the carbonyl or thiocarbonyl frequency positions as compared to sodium thiobenzoate was used to conclude preferential coordination to sulphur, or oxygen or both in the series of complexes. Following this procedure for the present complexes, the $\nu(\mathrm{C\overset{\cdots}{-}O})$ band at 1465 cm^{-1} and 1487 cm^{-1} is lower than the $\nu(\mathrm{C\overset{\cdots}{-}O})$ value of 1500 cm^{-1} for the salt. The $\nu(\mathrm{C\overset{\cdots}{-}S})$ bands at 963 cm^{-1} and 974 cm^{-1} are comparable to the value of 960 cm^{-1} for the sodium salt. Such results may indicate that although there is bidentate coordination a slight preference towards oxygen is exhibited. In compounds where there are S-bonded monothiocarboxylate groups the $\nu(C{=}O)$ frequency is above 1630 cm^{-1}. For example the compound $Me_2Ga(OSCMe)\cdot py$ has a $\nu(C{=}O)$ stretch of 1652 cm^{-1} and $\nu(\mathrm{C\overset{\cdots}{-}S})$ stretch of 642 cm^{-1} [132] and the compounds $Me_3SbX(SCOR)$ X = Cl, Br, R = Me, Ph have strong $\nu(C{=}O)$ bands in the region 1626-1644 cm^{-1}.[133] Clearly this is not the case in the present complexes.

NMR Spectral Data

There is little NMR data on transition metal carboxylates as most compounds are characterized by infrared, electronic, mass spectral, and magnetic data as well as structural studies. NMR data have been reported for the diamagnetic compound, $Cp_2Nb(O_2CCMe_3)$[120] and the trimethyltantalum(V) acetate complex, $Me_3Ta(O_2CMe)_2$.[134] The latter complex exhibits infrared bands for bidentate ligands (ν_{asym}(CO), 1520s, ν_{sym}(CO), 1400s) which results in the tantalum centre having a coordination number of seven. The NMR spectrum at 35°C consists of a singlet at δ1.55 for the acetate ligand and a singlet at δ2.38 for the methyls bonded to Ta. Lowering the temperature, to -80°C, caused the methyl resonance to broaden, however the acetate resonance remained sharp. In comparison to a series of other $Me_3Ta(chelate)_2$ compounds, this NMR behavior was considered indicative of fluxional behavior in the compound.

The NMR results for the present compounds that gave reliable spectra are listed in Table XVII. As mentioned before shifts from the diamagnetic values are expected for these paramagnetic uranium(IV) complexes. There is very little that can be said about the magnitude of the shifts in the absence of structural and magnetic studies. It is nevertheless worth pointing out that for the mixed amide-carboxylate complex, $Cp_2U(NEt_2)(O_2CCMe_3)$, the shifts are much larger than usually found in the Cp_2U type complexes.

As described in the previous chapter the monomeric $Cp_2U(chelate)_2$ type compounds possessing the pseudo-octahedral structure can in principle exist as the cis

Table XVII: ^{1}H NMR Data for $Cp_2U(carboxylate)_2$ Complexes

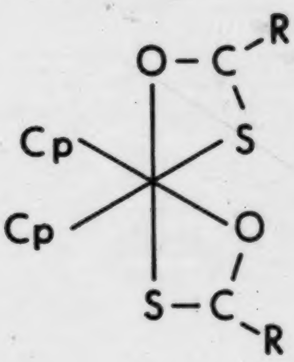
	Chemical Shift[a]			
Compound	Cp	CH_3	CMe_3	Other
$Cp_2U(OSCPh)_2$	1.2s (Cp and ortho protons)			-.6br(para), 1.6t(meta)[b]
$Cp_2U(OSCMe)_2$	1.0 s	11.7 s		
$Cp_2U(O_2CCMe_3)_2$	3.7 s		11.7s	
$Cp_3(O_2CCMe_3)$	12.9 s		18.2 s	
$Cp_2U(NEt_2)(O_2CCMe_3)$	32.4 s		14.2 s	-32.2 q(CH_2), -14.7t(CH_3)

[a] Relative to internal benzene; negative shift is a downfield shift. Temp = 35°C.

[b] See text for explanation.

and trans geometrical isomers. It was argued that based on some analogous compounds where the structure has been established, the above mentioned type of uranium derivatives most probably possess the cis octahedral geometry. This coordination geometry will be assumed in the present context also, in order to discuss the ^{1}H NMR spectra of the monomeric thiocarboxylate derivatives. Although it must be noted again that the trans form cannot be excluded based on the present set of data.

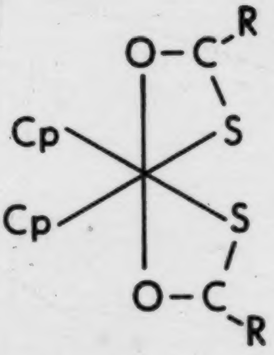
For these complexes three isomers are possible as outlined in diagrams 9a, b, c. Indicated in parentheses



9a

(2 Cp)

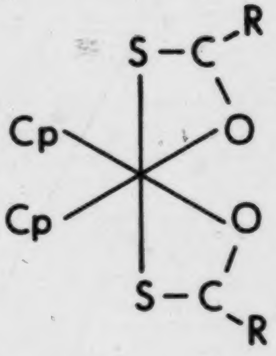
(2 R)



9b

(1 Cp)

(1 R)



9c

(1 Cp)

(1 R)

are the number of Cp and R group resonances expected for each isomer. If all three isomers were present in solution, then a complicated NMR spectrum should be observed. The ambient temperature ^{1}H NMR spectrum in C_6D_6 of the thioacetate complex exhibited two singlets due to the Cp ring and methyl group, the thiobenzoate derivative gave one singlet for the pentahapto cyclopentadienyl moiety and showed only the para and meta proton peaks of the phenyl ring. The simple spectra may be the result of accidental chemical shift equivalence or some non-rigid behavior akin to the processes detailed in the previous chapter. In order to distinguish between the two possibilities the variable temperature ^{1}H NMR behavior of $Cp_2U(OSCPh)_2$ was studied in CD_2Cl_2. The room temperature spectrum in this solvent showed only two peaks attributed to the Cp and para phenyl protons, although the integration was 8.8:1 instead of 5:1, indicating that some of the resonances were overlapping with that of the Cp ring. As the temperature was lowered the ortho and meta proton resonances became visible as they shifted away from the strong Cp signal. In Figure XII is shown the spectrum at -60°C. The assignments of the peaks were confirmed by selective decoupling experiments. A graph of the chemical shift of the protons versus 1/T is given in Figure XIII. This graph clearly illustrates the shifting of the ortho, meta and Cp proton resonances into the same area at ambient temperature. The peak positions are also affected slightly by solvent as is illustrated in Figure XIV. The NMR spectra of $Cp_2U(OSCPh)_2$ in three different solvents show the varying distance between the Cp and para proton peak positions (2.68 ppm CS_2, 1.78 ppm

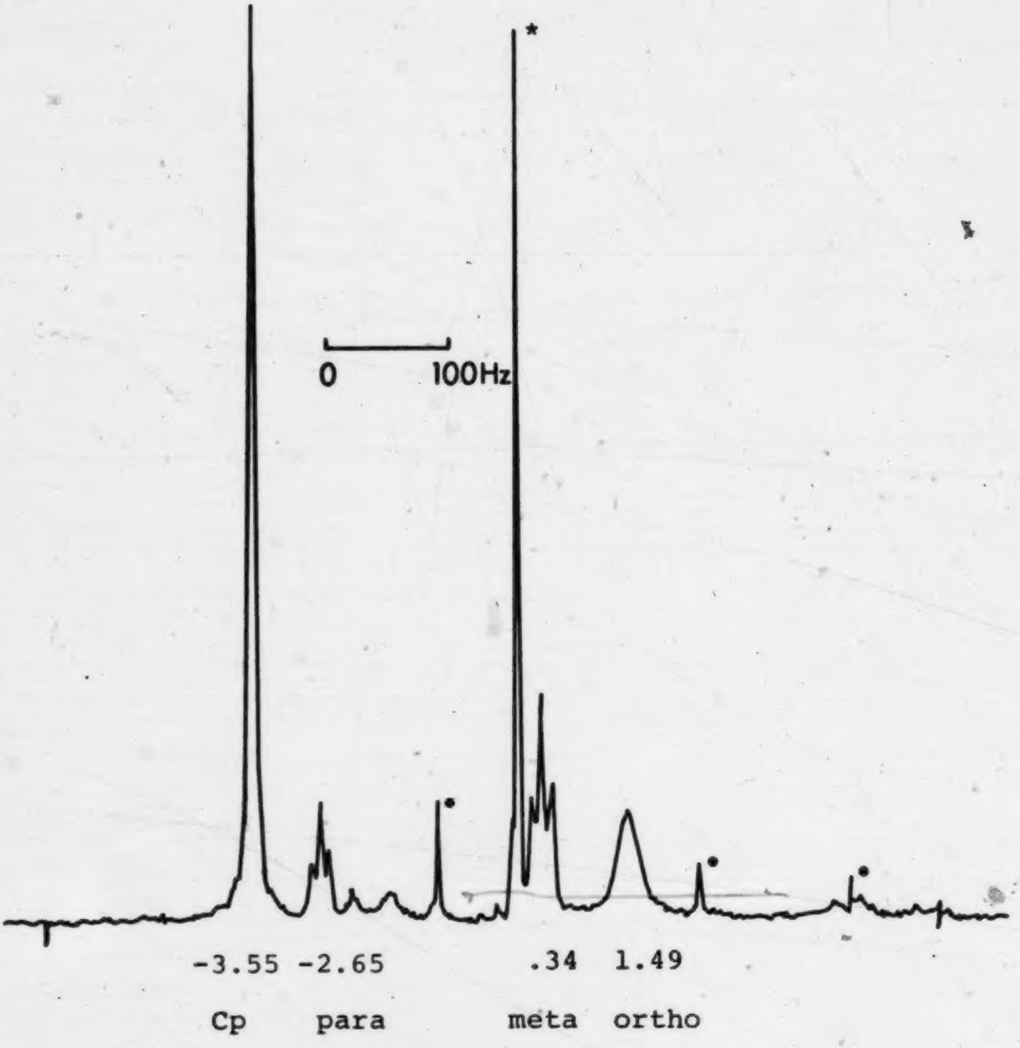


Figure XII: ^{1}H NMR Spectrum of $Cp_2U(OSCPh)_2$ at -60°C.

*CH_2Cl_2, chemical shifts in ppm from this peak.

•impurity.

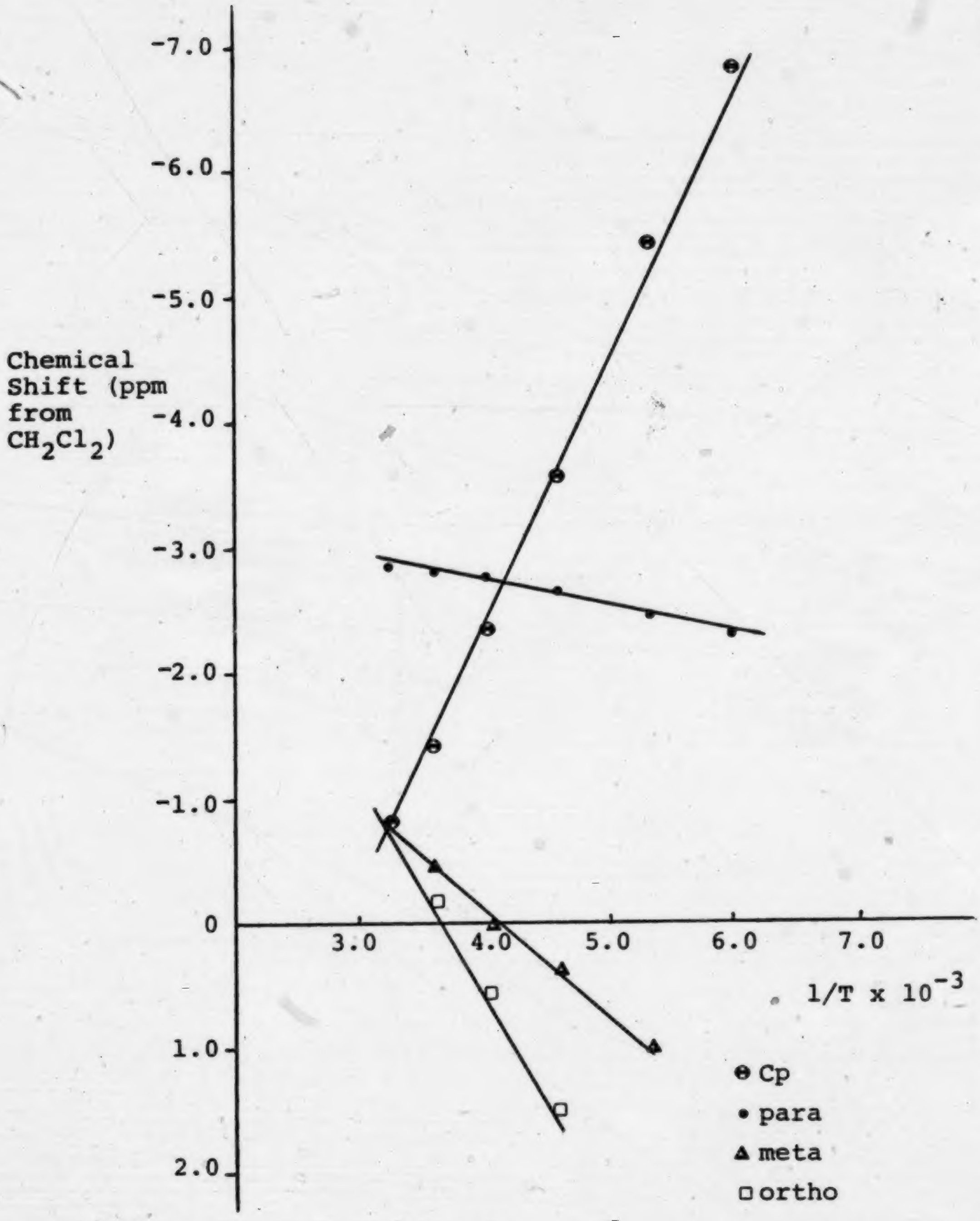


Figure XIII: Chemical Shift of Protons of $Cp_2U(OSCPh)_2$ versus 1/T.

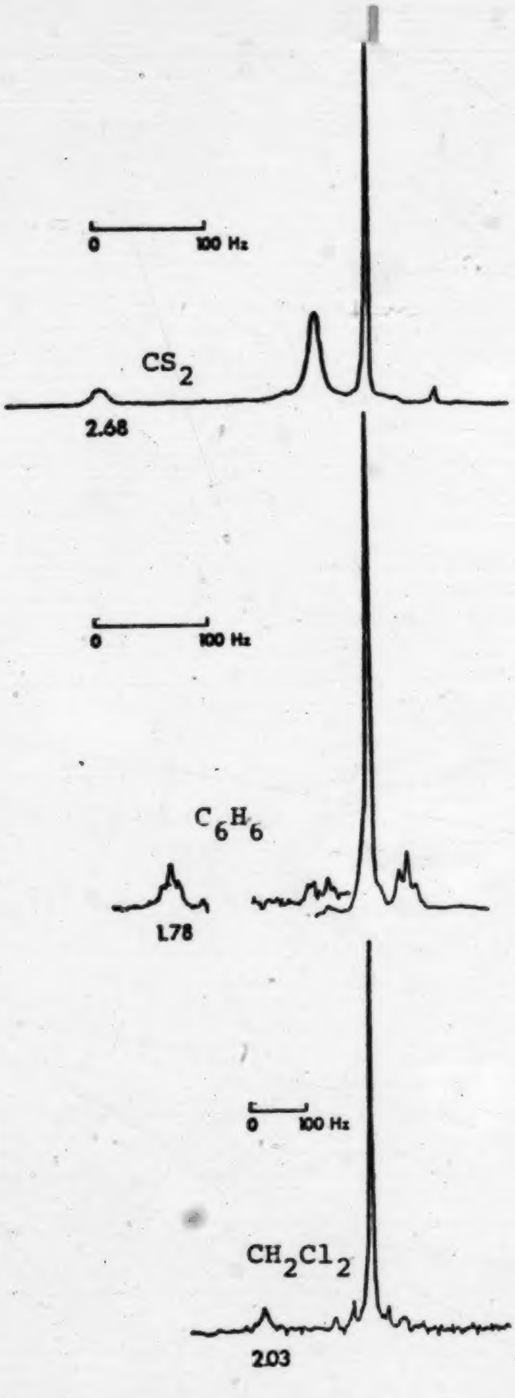


Figure XIV: ^{1}H NMR Spectra of $Cp_2U(OSCPh)_2$ in Various Solvents.

Chemical Shift of para protons in ppm from Cp resonance. CS_2, CH_2Cl_2: Temp = 35°C, C_6H_6: Temp = -32°C.

benzene and 2.03 ppm CD_2Cl_2).

These results are important for two reasons. First, they vividly demonstrate the potential danger of obtaining the NMR spectrum of a paramagnetic compound only at one temperature, since troublesome and unexpected overlap of resonances can sometimes occur. However they also clearly show that such accidental overlap can easily be determined from a variable temperature study since the temperature dependence of the chemical shifts for different protons or isomers are usually different. This last point seems to indicate that the observation of a single Cp resonance and one set of phenyl peaks for $Cp_2U(OSCPh)_2$ at -60°C is not due to accidental overlap of the resonances from different isomers but to some metal centered rearrangement that apparently interconverts the isomers even at this low temperature. As with the thiocarbamate complex discussed before, it is not known whether this is a simple trigonal-twist type position which would interconvert isomers 9b and 9c only or a more complicated process which would cause exchange amongst all three isomers. Furthermore it is important to realize that a metal centered rearrangement alone cannot produce the simple phenyl proton pattern observed at -60°C. Although interconverting isomers and R groups, such a motion does not exchange the two ortho and meta protons of the same phenyl ring. To do this C-Ph bond rotation must also be occurring.

Surprisingly in this complex bond rotation appears to be a higher energy process than metal-centered rearrangement. Indeed as the temperature is lowered from -60°C the peaks due to the ortho and meta protons broaden considerably and by -110°C both have disappeared into the baseline, whereas the Cp resonance remains a relatively sharp singlet and the para proton peak maintains its triplet appearance. Unfortunately since the low temperature limiting spectrum was not obtained, the energetics of the process could not be determined, nor can a definitive answer as to the stereochemistry of the complex be given.

The only carboxylate complex that dissolved sufficiently in benzene or in other non-donor solvents for ^1H NMR investigation was the pivalate derivative. The other carboxylates dissolved only in pyridine. Problems associated with running the NMR spectra in this solvent were mentioned already and will be discussed later on.

A molecular weight determination in benzene for $Cp_2U(O_2CCMe_3)_2$ indicated dimeric behavior and infrared data were consistent with bidentate carboxylate groups. It was of interest to see whether more information on the coordination geometry around the uranium could be gathered from the solution NMR data of the complex. Surprisingly the ^1H NMR spectrum at room temperature showed only two singlets in a 5 to 9 ratio due to the pentahapto cyclopentadienyl rings and the t-butyl groups respectively. The simple spectrum can be rationalized in at least three ways: the molecule possesses a highly symmetrical carboxylate bridged dimeric structure, some of the resonances are accidentally chemical shift equivalent at room temperature, or there is a rapid dimer $\rightleftarrows$ monomer equilibrium which averages the different resonances. As noticed before, the chemical shifts of paramagnetic complexes are temperature dependent, thus it is highly unlikely that peaks that are overlapping at room temperature will remain so as the temperature is varied, an excellent illustration has just been provided by the $Cp_2U(OSCPh)_2$ complex. In addition, the variable temperature NMR study might also establish the presence of the above indicated equilibrium.

The NMR spectrum of $Cp_2U(O_2CCMe_3)_2$ was recorded over the temperature range -90 to +90°C. The spectrum remained constant except for a slight broadening of the resonances and shifting of the peaks as expected for a paramagnetic compound. The temperature invariant nature of the NMR spectra clearly rules out accidental chemical shift equivalence as being responsible for the simple two line spectrum. Although rapid equilibrium at all temperatures with a small concentration of monomeric $Cp_2U(O_2CCMe_3)_2$ is possible, it is interesting to point out that in the case of $CpTi(O_2CPh)_2$ a symmetric dimeric structure has been established,[125] Figure XVa. Recognizing the larger size of uranium and its propensity for high coordination number, a closely related structure but with two cyclopentadienyl groups on the uranium, Figure XVb, might not be an unreasonable postulate for the structure of $Cp_2U(O_2CCMe_3)_2$.

The other carboxylate derivatives, $Cp_2U(O_2CPh)_2$ and $Cp_2U(O_2CMe)_2$ were insoluble in all non-donor solvents, but they were soluble in pyridine. However the appearance of the NMR spectra for these compounds as well as $Cp_2U(O_2CCMe_3)_2$ and $Cp_2U(OSCMe)_2$ in pyridine-d_5 has not been totally analyzed. It seems that small amounts of water in the solvent have caused hydrolysis, since peaks due to cyclopentadiene were observed in all four cases.

An NMR spectrum of a sample containing a 80:20 mixture of $Cp_2U(O_2CCMe_3)_2$ and $Cp_3U(O_2CCMe_3)$ exhibited peaks whose integration agreed with a mixture containing $Cp_2U(O_2CCMe_3)_2$ and a molecule with formula "$Cp_2U(O_2CCMe_3)$". An integration for $Cp_3U(O_2CCMe_3)$ was not obtained. It is postulated that hydrolysis of the $Cp_3U(O_2CCMe_3)$ compound occurred as in the following equation.

$$Cp_3U(O_2CCMe_3) \xrightarrow[pyr]{H_2O} Cp_2U(O_2CCMe_3)(OH)\cdot pyr + CpH \quad (IV\text{-}4)$$

The hydroxyl proton was not seen in the NMR region scanned. However an extremely large shift would be expected for this proton since other uranium(IV) complexes show large

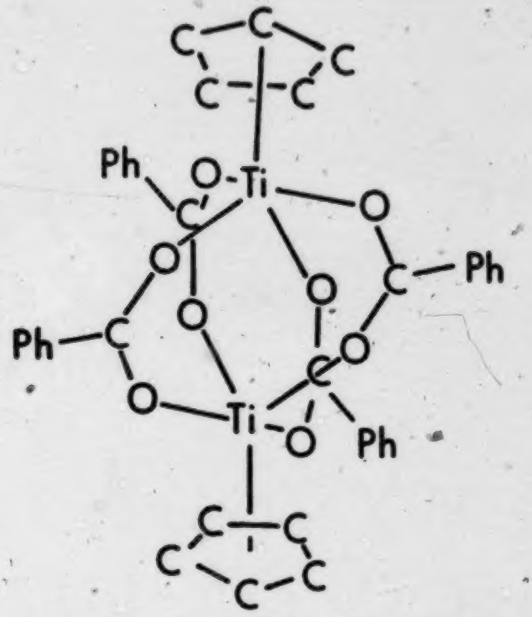

C
C
C
C
C
Ph
O-Ti
C
O
O
O
C
Ph
Ph
C
O
O
C
O
Ti
O
Ph
C
C
C
C
C

Figure XVa: Dimeric Structure of CpTi$(O_2CPh)_2$

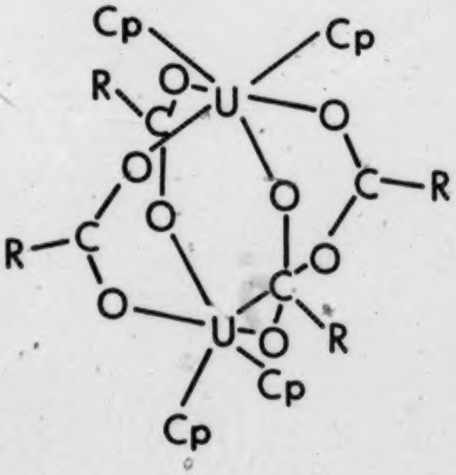

Cp
Cp
R
O-U
C
O
O
O
C
R
R
C
O
O
C
O
U
O
R
Cp
Cp

Figure XVb: Postulated Dimeric Structure of $Cp_2U(O_2CCMe_3)_2$

R = CMe_3

shifts for a proton one atom away from the metal centre.[10] The peak corresponding to the Cp protons of "$Cp_2U(O_2CCMe_3)$" was observed at approximately 58 ppm above pyridine.

In a study of the compound $Cp_2U(O_2CPh)_2$ dissolved in pyridine, a peak assumed to be due to the Cp protons was observed at 77 ppm below internal pyridine. It is unlikely that simple coordination of pyridine to the $Cp_2U(O_2CPh)_2$ molecule is causing this large shift since the NMR spectrum of the adduct of the compound $U(CF_3COCHCOOEt)_4$ with pyridine did not show such large displacements as indicated above.[135] A more probable reason for the chemical shifts is that the donor solvent pyridine is promoting a rearrangement to other uranium(IV) species. As mentioned in a previous section a mass spectral analysis of the solid resulting from a solution of $Cp_2U(O_2CMe)_2$ and pyridine indicated the presence of mainly $CpU(O_2CMe)_3$. It is possible that a similar monocyclopentadienyl compound is formed in the benzoate case. Further substantiation for this rationale is provided in the next section where the ^1H NMR spectrum of $CpU(O_2CCMe_3)_3$ exhibits a strong peak at 23 ppm below internal dichloromethane.

In summary the interpretation of the ^1H NMR data in pyridine consists of a hydrolysis reaction to produce both a cyclopentadiene and Cp_2U containing species and a possible rearrangement of the complexes to mono(cyclopentadienyl) derivatives stimulated by the properties of the donor solvent pyridine itself.

Mono(cyclopentadienyl)tris(carboxylato)uranium(IV).

There are only a few mono-cyclopentadienyl uranium compounds known, $CpUCl_3 \cdot dme$,[23] $CpUCl_3 \cdot 2THF$,[136] $CpUCl_2[HB(N_2C_3H_3)_3]$[137] and the oxygen-donor complexes of $CpUCl_3$ and $CpUBr_3$ of the type $CpUX_3L_2$ and $[CpUX_3L]_2$.[20] The synthesis of another CpU type compound would be informative especially of the type $CpU(chelate)_3$ since it would be expected to have a seven-coordinate uranium centre. A recent report of the seven-coordinate zirconium complexes, $CpZr(S_2CNR_2)_3$, R = Me, Et stated that stereochemically rigid NMR behavior was observed for these compounds at ambient temperature.[138] This result is contrasted to the seven-coordinate $Zr(acac)_3Cl$[139] which undergoes fluxional processes even at low temperatures. In view of this difference, the study of the seven-coordinate uranium species would be interesting.

The preparation of $CpU(O_2CCMe_3)_3$ followed the same general procedure as given in equation (II-2) except that three equivalents of acid were used. A mass spectral analysis on the pale green solid isolated from the reaction mixture showed fragment peaks from $CpU(O_2CCMe_3)_3$ almost exclusively. Less than 2% of the compound $Cp_2U(O_2CCMe_3)_2$ was observed.

The infrared spectrum of $CpU(O_2CCMe_3)_3$ is comparable to that of $Cp_2U(O_2CCMe_3)_2$ as is shown in Figure XVI. The

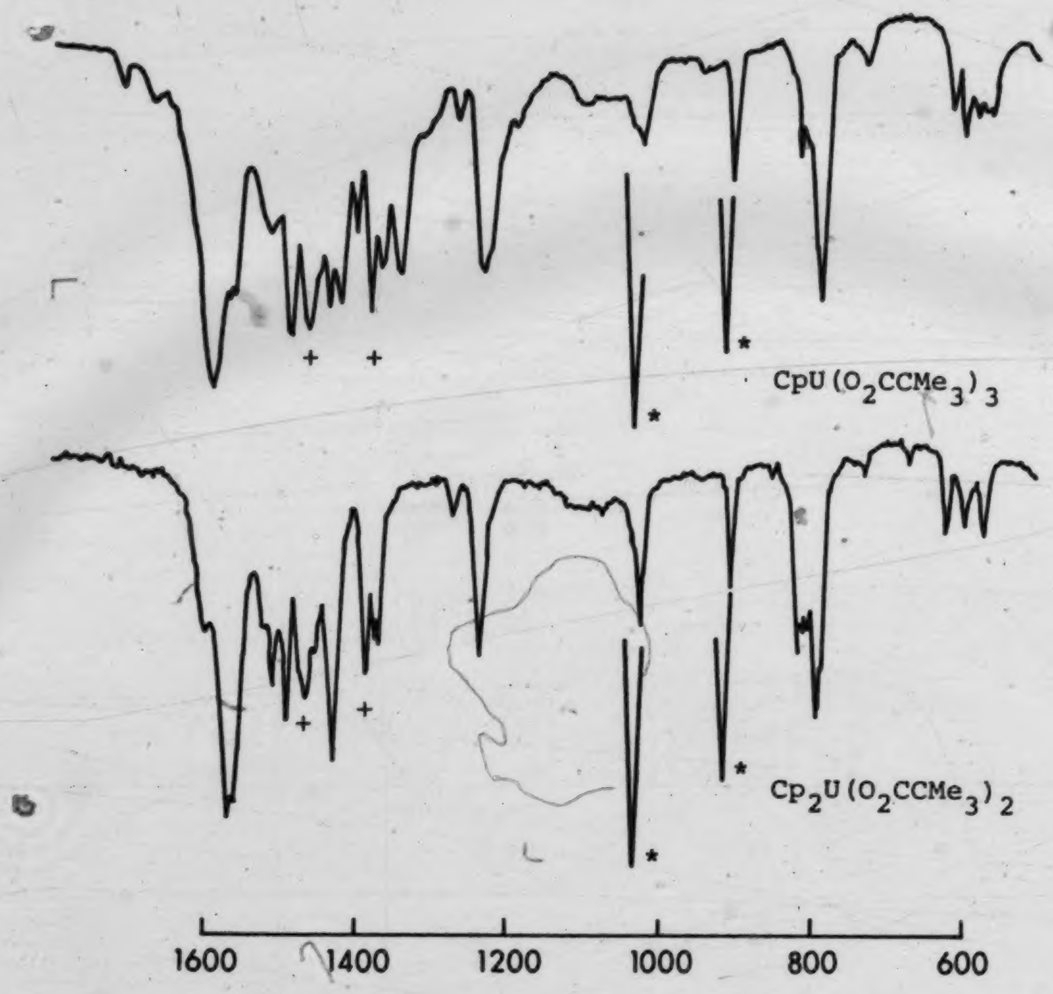


Figure XVI: Infrared Spectra of $CpU(O_2CCMe_3)_3$ and $Cp_2U(O_2CCMe_3)_2$.

*polystyrene.

+Nujol.

assignment of $\nu_{asym}(CO)$ at 1582 cm^{-1} and $\nu_{sym}(CO)$ at 1480 cm^{-1} would give a $\Delta\nu$ value of 102 cm^{-1} indicative of symmetric coordination. In the absence of any molecular weight data it is not possible to state whether the coordination is bidentate or bridging.

It seemed from the spectroscopic data collected above that the desired compound had been obtained. However the NMR spectroscopic results are less than satisfactory. An NMR spectrum of the solid exhibited only broad peaks centered around 8 ppm above internal CH_2Cl_2 as well as two upfield decomposition peaks which have been observed before in impure samples of $Cp_2U(O_2CCMe_3)_2$. Judging from NMR spectra of other $Cp_2U(IV)$ complexes which have shown broad peaks at room temperature, the rather featureless appearance of this spectrum was not very surprising. It was assumed that in this case some fluxional process was occurring which resulted in broadening of the resonances The variable temperature NMR study was done, however the spectra could not be assigned as the integration of the peaks observed did not correlate with any reasonable chemical formulation. The spectrum at -75°C consisted of three main peaks at 31.5 ppm and 23.7 ppm below CH_2Cl_2 and 21.9 ppm above CH_2Cl_2. The peaks at 23.7 ppm and 21.9 ppm grew in from the baseline as the temperature was lowered. The integration for these peaks was 5:10:30 respectively. Clearly some fast process has become slower as the temperature is lowered. It is possible that the limiting spectrum has not been reached and this could account for the poor fit of the integration data (for a static pentagonal bipyramidal structure a ratio of 5:9:18 is expected). It would be worthwhile to repeat the experiment on a pure sample of the compound.

These very preliminary results do indicate that for $CpU(O_2CCMe_3)_3$ there may exist stereochemical lability, a result that is also observed in related transition metal analogues. For example, $CpZr(O_2CMe)_3$,[114] exhibits two sharp peaks in the ^1H NMR at δ6.26 for the cyclopentadienyl ring and δ1.73 for the methyl protons. It seems that for this type of compound there is a close similarity in the structural behavior between the uranium and transition metal cases.

Conclusions

The reaction of the reagent $Cp_2U(NEt_2)_2$ with carboxylic and thiocarboxylic acids has provided a facile route to $Cp_2U(\text{carboxylate})_2$ derivatives. The compounds showed a variation of associated behavior which was dependent both on the organic group of the acid and the sulphur and oxygen functionalities. The compound $Cp_2U(OSCPh)_2$ is a monomer whereas the compound $Cp_2U(O_2CPh)_2$ is considered a polymer due to its insolubility in organic solvents. Changing the organic group from phenyl to tertiary-butyl resulted in formation of the soluble dimeric compound

$Cp_2U(O_2CCMe_3)_2$.

The infrared data showed that the cyclopentadienyl groups were bonded in a pentahapto fashion and that the carboxylate and monothiocarboxylates were attached in a symmetrical manner to the metal. However it was not possible to say conclusively whether bridging ligands were present based on the infrared data alone. Certainly in the case of the pivalate complex where molecular weight data showed dimeric behavior, bridging carboxylate groups could be assumed.

The ^1H NMR study of $Cp_2U(O_2CMe_3)_2$ suggested that all four carboxylate groups were bridging as only one chemical environment was indicated. The ^1H NMR data for $Cp_2U(OSCPh)_2$ was interpreted as suggesting a cis octahedral structure possessing non-rigid behavior. Stereochemical non-rigidity was also postulated for $CpU(O_2CCMe_3)_3$ to account for the low temperature ^1H NMR spectrum. The large chemical shifts observed for the complexes in the solvent pyridine were suggested as arising from a monocyclopentadienyl type complex formed from possible rearrangement processes stimulated by the pyridine solvent.

The tendency of uranium to achieve higher coordination numbers, as seen before for the inserted products, is also controlling the stereochemistry of the compounds here. The attainment of a $Cp_2M(chelate)_2$ type complex is a significant departure from the situation of analogous transition metals.

As also noted before, the spectroscopic data do not provide an answer to the question of the exact stereochemistry about the uranium centre. Obviously structural studies would have to provide this information.

CHAPTER FIVE

METALLA-ACETYLACETONATE DERIVATIVES OF BIS(CYCLOPENTADIENYL)URANIUM(IV)

Introduction

One area of actinide chemistry that has been investigated for a long time concerns derivatives of acetylacetone, with one of the earliest reported compounds being Th(acac)$_4$.[140] The acetylacetonate ligand, and its derivatives, possess some of the same properties as the carboxylate group, which accounts for its widespread use.[141] These include the ability to vary the coordination mode (monodentate, bidentate, bridging), and to stabilize higher oxidation states of metals.[142] As well, the larger bite of the acac ligand allows for less distortion in structures while spanning different coordinate positions.

A considerable amount of work on U(β-diketonate)$_4$ compounds was initiated as part of the Manhattan Project and published by Gilman in 1956.[143] The great interest in β-diketonate compounds then and to a lesser extent now, arises from their volatility, a property essential for certain separation techniques.[144,145] One of the derivatives has also been considered for use as an NMR chemical shift reagent.[146] The compound tetrakis-(1,1,1-trifluoro-4-phenylbutane-2,4-dionato)uranium formed adducts with pyridine and n-butyl alcohol and as a result the peak positions of the organic substrates were shifted.

While there are numerous organometallic derivatives of transition-metal elements, compounds containing two cyclopentadienyl and two β-diketonate ligands are unknown. The compound $Cp_2U(acac)_2$ has been synthesized but as yet has not been fully characterized.[147,148]

A recent development in β-diketone chemistry has been the preparation of a metalla-β-diketone molecule, cis-$(OC)_4Re(MeCO)_2H$,[149] a metalla-analogue of acetylacetone. The acidity of the rhenium complex was stated to be similar to that of acetylacetone.[150] It was concluded that reactions of the reagent $Cp_2U(NEt_2)_2$ with the metalla-acetylacetone molecule stated above as well as other substituted derivatives would undergo substitution reactions analogous to the carboxylates as shown in equation (V-1).

$$Cp_2U(NEt_2)_2 + 2(CO)_4Re[(MeCO)(RCO)]H \longrightarrow Cp_2U[cis\text{-}(OCMe)(OCR)Re(CO)_4]_2 + 2HNEt_2 \qquad (V\text{-}1)$$

Reactions of these rhenium complexes with a variety of main group[151] and transition metal compounds[152] have been investigated and their products characterized by NMR and infrared spectroscopy. The comparison of these parameters and others from acetylacetonate derivatives to the uranium complexes should prove to be interesting.

Results and Discussion

Synthetic Aspects

The rhenium metalla-acetylacetone and its substituted derivatives are considered analogues of the enol tautomer of acetylacetone since the X-ray structure of cis-$(CO)_4$-$Re[MeCO]_2H$ showed that the hydrogen was bonded to the acyl-carbonyl oxygens and not to the rhenium atom.[150] The reaction chemistry of the rhenium-enol complexes would be expected to show some of the same reactivity as do acetylacetones. The acidic nature of these complexes was confirmed by the reaction with the reagent $Cp_2U(NEt_2)_2$ as shown below:

$$Cp_2U(NEt_2)_2 + 2(CO)_4Re[(MeCO)(RCO)]_2H \longrightarrow Cp_2U[cis\text{-}(OCMe)(OCR)Re(CO)_4]_2 + 2HNEt_2 \qquad (V\text{-}2)$$

$R = Me, CHMe_2$

The reaction of the symmetrical rhenium-enol, (R = Me), at 0°C in hexane solvent produced the expected bis-substituted product in almost quantitative yield. The compound could be crystallized from a toluene/hexane, or CH_2Cl_2/hexane solvent mixture. It can also be sublimed although not very efficiently. The mass spectral analysis of the residue showed only the presence of $Re_2(CO)_{10}$. Analytically pure compound can be obtained from the initial precipitation in the hexane reaction mixture.

The unsymmetrical rhenium-enol, R = $CHMe_2$, also underwent the same substitution reaction at 0°C in hexane, but the formed product did not precipitate out of the solution. The greater solubility of this compound coupled with its inability to undergo sublimation without decomposition made isolation of a pure product difficult, a goal which has still not been attained at the present time. Hence the discussions following will concern mainly the symmetrical compound.

Infrared Spectral Data

The coordination about the uranium centre can be determined from the infrared spectral data. The characteristic infrared frequencies of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ are given in Table XVIII. The four carbonyl resonances at higher wavenumbers are expected for a cis-$Re(CO)_4$ unit.[153] The assignment of interligand acyl $\nu(C\overset{\cdots}{—}O)$ stretching frequencies at 1529 cm^{-1} and 1499 cm^{-1}, together with a clear region between 1600 cm^{-1} and 1750 cm^{-1} of the acyl metal carbonyl functionality, indicate that the acyl carbonyl groups are bonded to the uranium metal resulting in a chelating metalla-acac moiety. The frequencies assigned to the cyclopentadienyl group are consistent with pentahapto bonding of the rings to the uranium.

In Table XIX are listed the carbonyl absorptions for the uranium compound and other metalla-β-diketone complexes.

Table XVIII: Characteristic Infrared Absorptions of $Cp_2U[cis-(OCMe)_2Re(CO)_4]_2$.[a]

Absorbance	Assignment
2081 m	$\nu(CO)$
2017 m	
1975 vs	
1938 vs	
1528 m	ν_{acyl} CO
1496 s	
1404 w	ν(C-C)Cp
1092 m	ν(C-C)Cp
1018 w	δ(C-H)Cp
786 s	γ(C-H)Cp

[a] 1600-450 cm^{-1} region, recorded in Nujol mull.

Table XIX: IR Spectral Data of Carbonyl Absorptions for Metalla-β-Diketonate Complexes (cm^{-1}).[a,b]

	ν(CO)	ν(acyl)	Ref.
cis-$(CO)_4Re(MeCO)H$	2096(m) 2010(vs) 1991(vs) 1956(vs)	1511(m)	150
$Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$	2081(m) 1988, 1977(vs) 1948(s)	1529sh 1499(m)	b
[cis-$(CO)_4Re(MeCO)(PhCH_2CO)]_3Al$	2070(m) 1988(vs,br) 1950(s)	1512(m)	149
[cis-$(CO)_4Re(MeCO)_2]BCl_2$	2120(m) 2040(vs) 2020(vs) 1987(s)	1447(m)	151
[cis-$(CO)_4Re(MeCO)_2]_2Cu$	2088(m) 1991(s) 1973(vs) 1965(s)	1506(m)	152

[a] In CH_2Cl_2 solvent.

[b] This work.

There is little variation among the positions of the terminal carbonyl absorptions and the acyl stretching frequencies of the compounds, with the exception of the boron derivative. The boron complex exhibits an acyl stretching frequency noticably lower than that of the other compounds. In a comparison to the uranium compound this shift is probably the result of stronger coordination of the metalla-acac ligand to the BCl_2 group than the Cp_2U moiety. The greater electronegativity of the boron centre compared to uranium contributes to an increased interaction of the acyl oxygen with boron. A comparison of metal-oxygen bond energies indicates that the boron-oxygen bond is stronger, 136 to 188 kcal/mole[154] compared to 66 kcal/mole for the uranium-oxygen bond of the acac ligand in $UO_2(acac)_2$.[155] It is interesting to note that the terminal carbonyl stretching frequencies also reflect this increased interaction. The greater drain of electron density from the rhenium in the boron complex renders the metal less effective in back bonding to the terminal carbonyl groups thus resulting in the observed increase in terminal carbonyl stretching frequencies.

The uranium complex has two acyl absorptions which could arise from the symmetric and asymmetric acyl stretching modes of the chelating metalla-acac ligands. Both vibrational modes are expected to be infrared active in the low symmetry structure, C_2, arising from cis orientation of the Cp and metalla-acac ligands *(vide infra)*.

Mass Spectral Data

The mass spectral data for $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ and $Cp_2U[cis\text{-}(OCMe)(OCCHMe_2)Re(CO)_4]_2$ are listed in Table XX. The table only shows the uranium containing fragments and indicates the highest peak of a multi-isotope fragment although the expected isotope patterns were observed in all cases. It should also be noted that peaks corresponding to the stepwise loss of up to nine carbonyls from the fragment $(P\text{-}Cp)^+$ were observed, the listing of only two of these peaks in the table is for purely economic reasons.

The parent ion is observed at the lower temperature (120°C) for both complexes indicating that the molecular framework possess a fair degree of stability for such large carbonyl containing species. The bulky metalla-acac ligand does have an effect compared to the purely organic acac ligand as a mass spectrum of $U(acac)_4$ has a relative abundance of approximately 30% for the parent ion.[156] As well the mass spectrum of a mixed chelate complex, $U(salen)(acac)_2$, [salen = N,N'-ethylenebis-(salicylideneiminato)], also exhibited a very intense parent ion (relative intensity 50% of uranium-containing fragments.)[157] The presence of the molecular ion for the symmetrical compound is quite dependent upon the

Table XX: Uranium-Containing Fragments in the Mass Spectra of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ and $Cp_2U[cis\text{-}(OCMe)(OCCHMe_2)Re(CO)_4]_2$.

Proposed Assignment	$Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$				$Cp_2U[cis\text{-}(OCMe)(OCCHMe_2)\text{-}Re(CO)_4]_2$	
	Mass m/e	Relative[a] Abundance (%)	Mass m/e	Relative[b] Abundance (%)	Mass m/e	Relative[b] Abundance (%)
Parent $(P)^+$	1136	0	1136	13.6	1192	4.5
$(P-CO)^+$	1108	7.4	1108	.1	1164	0
$(P-OCMe)^+$	1093	2.9	1093	0	1149	64.4
$(P-OCCHMe_2)^+$					1127	100
$(P-Cp)^+$	1071	0	1071	100	1121	3.2
$(P-CO-Cp)^+$	1043	82.9	1043	5.7	1099	16.2
$(P-9CO-Cp)^+$	819	12.6	819	13.2	875	12.8
$(P-Re\text{-}enol)^+$	753	18.7	853	26.1	781	76.9
$(CpU(OC)_2(OCH)_2)^+$	417	43.7	417	57.1	417	17.1
$(CpU(OC)_3)^+$	387	100	387	2.9	387	6.4
most abundant peak	371	$[(CO)_4Re(OCMe)(OCH)]^+$	1071	$(P-Cp)^+$	299	$[(CO)_3ReCHMe]^+$

[a] T = 140°C. [b] T = 120°C.

probe temperature. A significant amount of the P^+ ion is seen at 120°C, but none is observed at 140°C. The high temperature clearly causes breakup of the compound as is evident from the composition of the most abundant peak, which involves only the ligand. At the lower temperature, the most abundant peak is from the complex itself, a fragment that is not observed at the higher temperature.

The unsymmetrical compound, $Cp_2U[cis-(OCMe)(OCCHMe_2)-Re(CO)_4]_2$ having a bulkier metalla-β-diketonate ligand, experiences more breakdown from the parent ion. Loss of ligand (called $P-(Re\text{-}enol)^+$) is a major fragmentation pattern for this compound as compared to the symmetrical case where losses of cyclopentadienyl ring and carbonyl groups are prevalent. The most abundant peak is again due to a fragment from the ligand.

NMR Spectral Data

The ^1H NMR spectra of metal complexes containing β-diketonate ligands have been distinguished by their simple appearance, partly due to the fluxional behavior of many of the compounds investigated.[158] Among the metal systems which have been studied are those of the type $M(acac)_2XY$ where M = Zr, Hf, Ti, Sn; X, Y = monodentate ligands. An initial study of halogen derivatives, $Ti(acac)_2X_2$ where X = F, Cl, Br by Fay and Lowry[159] indicated that the complexes were in the cis octahedral isomeric form and were undergoing rapid configurational rearrangements. The cis isomer assignment was based on the ^1H variable temperature study which for $Ti(acac)_2Cl_2$ showed two methyl peaks at -50°C which coalesced into a single peak at 60°C. The methine proton resonance remained a sharp singlet at all temperatures. These results are only consistent for a cis isomer since the trans isomer would have identical environments for all methyl groups. A similar study with tin complexes, $Sn(acac)_2X_2$,[160] also concluded that they had a cis arrangement of ligands and underwent rearrangement processes, although the tin compounds are more rigid (higher activation energy) than the early transition metal complexes. For $Sn(acac)_2Cl_2$, two methyl resonances were seen at 44°C which coalesced to a single peak at 149°C. Extensions of this work include the alkoxy derivatives of β-diketonate titanium(IV) complexes[100] and chloroalkyl tin acetylacetonate derivatives.[99] In almost all cases, the cis isomeric form predominated in solution and the compounds exhibited intramolecular rearrangements.

A problem associated with the fluxional behavior is that the compounds may be so labile that the limiting spectrum may not be reached. This situation occured for the compounds $M(acac)_2X_2$ where M = Zr, Hf and X = Cl, Br.[139] The simple spectra were still maintained at -130°C. Very recently NMR results on the compounds Zr and $U(acac)_4$

gave coalescence temperatures of -45°C and -163°C respectively,[161] so rather labile systems can be anticipated.

The ^{1}H NMR spectrum of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ in toluene at ambient temperature exhibited one sharp peak at 3.3 ppm above TMS and a very broad hump, almost in the baseline, spread between the solvent peak and the peak at 3.3 ppm. However as the temperature is lowered two new peaks, at either side of the singlet observed at room temperature, emerge and sharpen up. This is diagramed in Figure XVII. The low temperature limiting spectrum is reached by -50°C as no more line shape changes are observed below that temperature. The ratio of the resonances at this temperature is 10:6:6 corresponding to the two cyclopentadienyl rings and the four methyl groups which are in two different environments. As the the temperature is raised from room temperature a broad peak appears at the high field side of the Cp resonance and sharpens slightly as the temperature reaches 100°C. Unfortunately, at the same time peaks due to decomposition also appear in the spectrum.* Decomposition becomes so extensive that recording the spectrum above 100°C was not

---

*This decomposition peak seen at 2.41 ppm above TMS (9.51 ppm from aromatic toluene), has been observed in many NMR samples which have been lett for a period of time. A mass spectral analysis of an NMR sample containing a large amount of this peak indicated that the decomposition may be due to the monocyclopentadienyl compound $CpU[cis\text{-}(OCMe)_2Re(CO)_4]_3$. The formation of this derivative is not surprising based on the trends seen in the last chapter on carboxylic acids, where structural changes to the monocyclopentadienyl complexes occured.

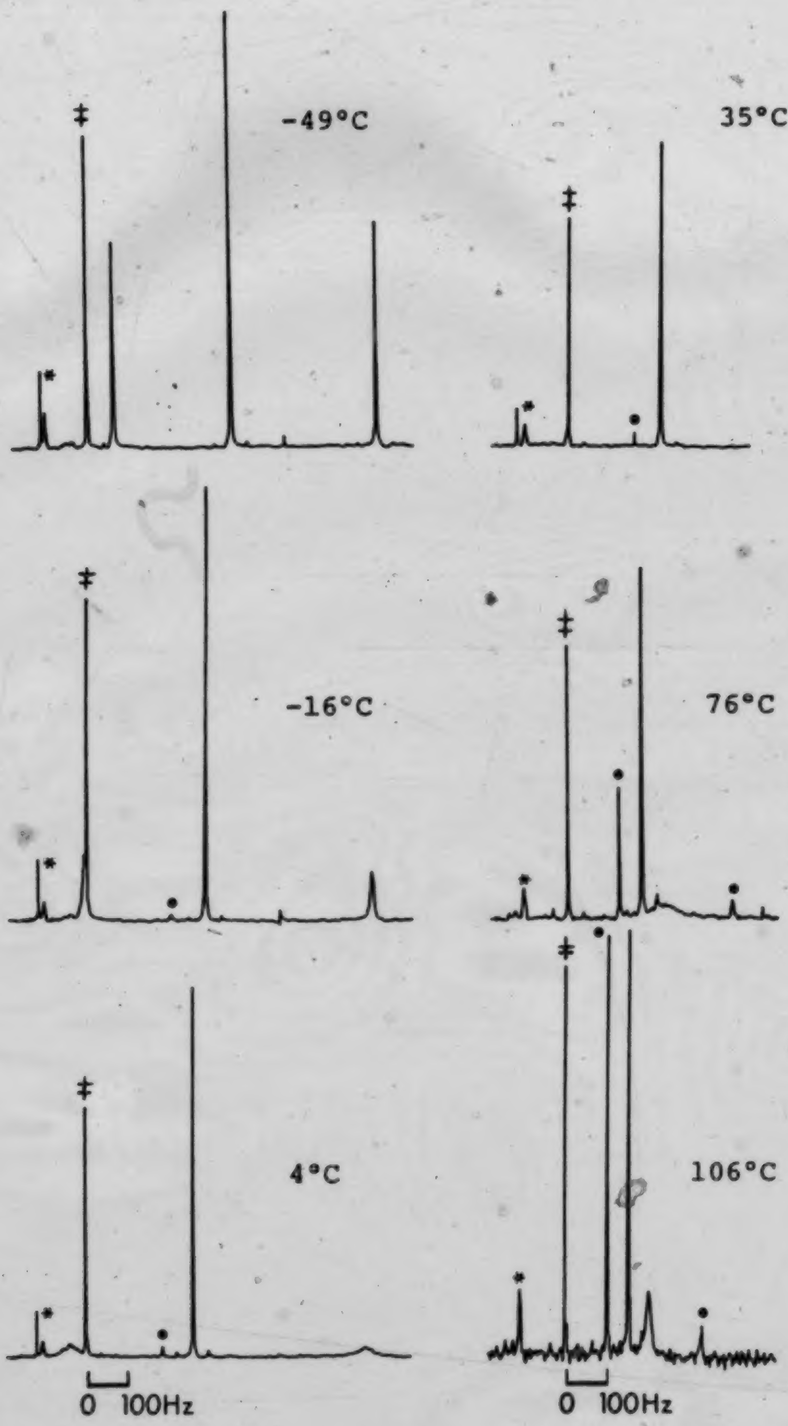


Figure XVII: ^{1}H Variable Temperature NMR Spectra of $Cp_2U[cis-(OCMe)_2Re(CO)_4]_2$.

*toluene, ‡grease, •decomposition.

feasible. Even though the high temperature limiting spectrum has obviously not been obtained and the integration of the two peaks at 100°C is not quite the expected 10:12 ratio, it is felt that the high field peak is due to the four methyl groups which are undergoing environmental averaging by some rearrangement processes. The reversible nature of the observed line shape changes also supports non-rigid behavior. It should be noted that the Cp resonance throughout the temperature range remains a sharp singlet and only undergoes changes in its chemical shifts as expected for a paramagnetic complex. Of course the chemical shifts of the methyl groups are also temperature dependent. This is shown in Figure XVIII in two solvents, CH_2Cl_2 and toluene. In the limited temperature range available, the plots exhibit linear behavior. However it is also apparent from the graphs that the chemical shifts are solvent dependent. Similar effects have been observed by Karraker *et al.*[6] for tetrakis(β-diketonate)uranium(IV) complexes. The cause for the solvent dependence, especially the fact that only one of the peaks seems to change significantly in the present complexes is not known. Nevertheless, the chemical shifts at any temperature can be obtained by extrapolation of the chemical shift versus temperature plots. This shows that in the absence of exchange at 100°C, two peaks at 11.3 ppm above and 2.7 ppm below

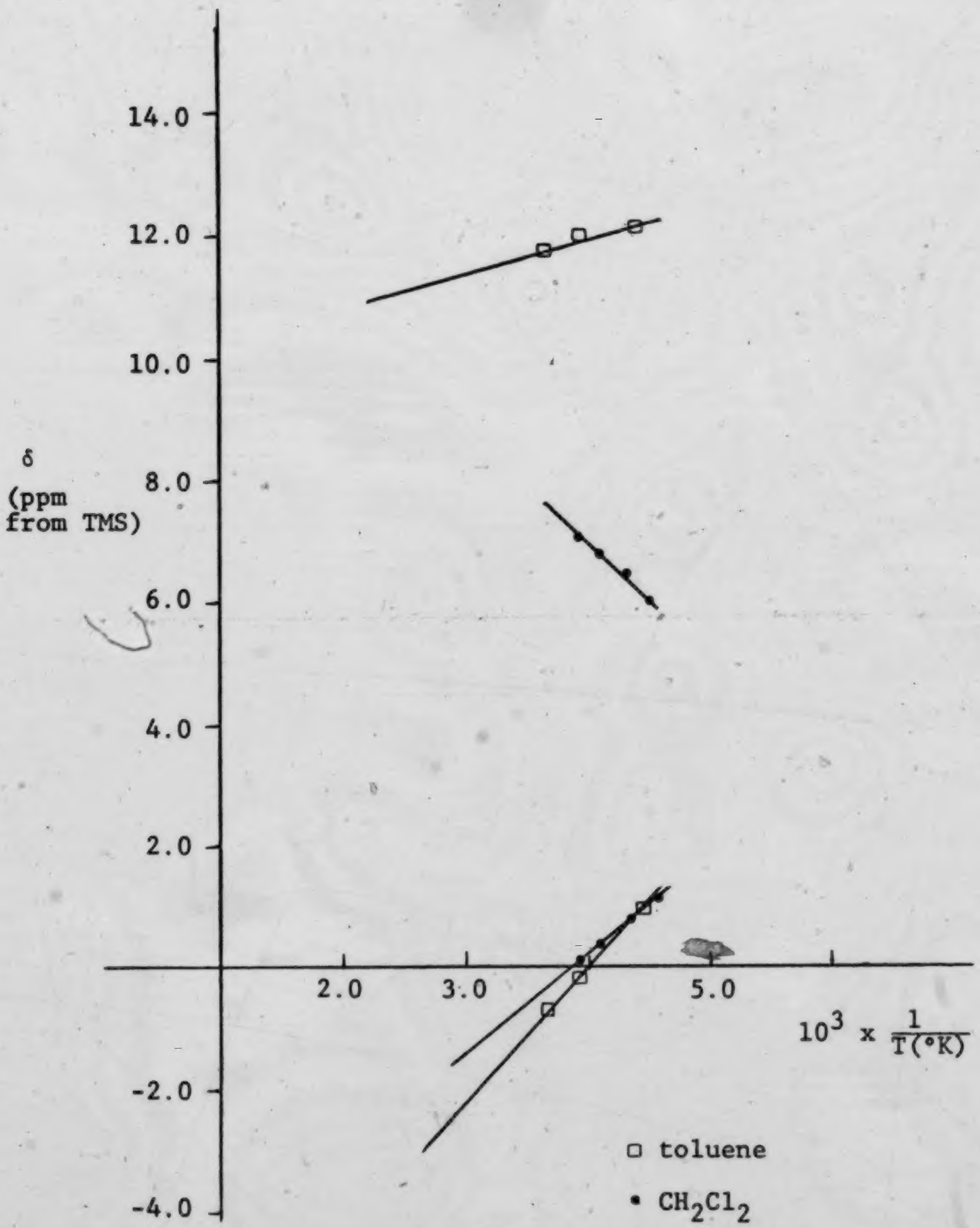


Figure XVIII: Chemical Shift of Methyl Protons of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ versus 1/T.

TMS should be observed. The average of these two values is 4.3 ppm above TMS. This is reasonably close, especially considering that the extrapolation is based on relatively few points, to the chemical shift of the peak at the high field side of the Cp resonance which occurs at 3.5 ppm above TMS. This rough calculation may be supportive of the postulate that the latter peak is due to the averaging methyl groups and that the rearrangement is intramolecular.

Before considering the mechanism for the rearrangement the ground state structure of the molecule must be established. The two possible geometric forms for the pseudo-six coordinate $Cp_2U(chelate)_2$ compounds are the cis and trans octahedral structures. In the present context, with a symmetrical chelate, the former has C_2 while the latter D_{2h} symmetry. Although in previous chapters the geometries of the molecules could not be deduced unequivocally, with the molecule at hand the low temperature ^1H NMR spectrum is only consistent with the cis octahedral form. The trans geometrical isomer having only one methyl environment is clearly not in accord with the NMR data. It is also noted that a preliminary structural result on $Cp_2U(acac)_2$ also indicated a cisoid arrangement of the cyclopentadienyl ligands.[162]

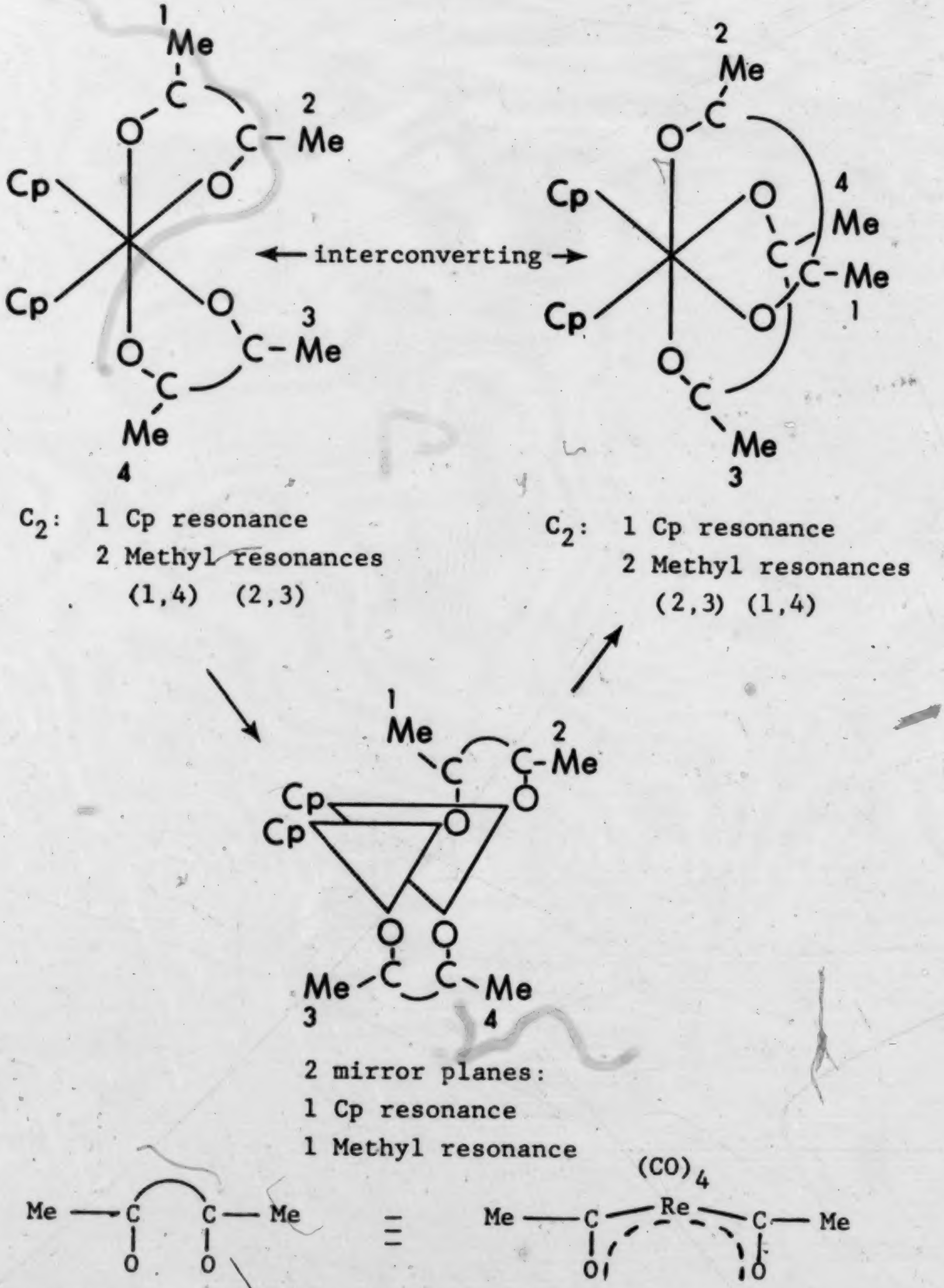
This molecule thus joins the large class of cis-$M(acac)_2X_2$ type compounds which exhibit fluxional behavior.

A possible explanation for the temperature dependent line shape changes is a trigonal-twist metal-centered rearrangement, a Bailar twist.[163] This is shown in Figure XIX.

At low temperature, the static structure would be the cis arrangement possessing a C_2 axis which interconverts the Cp groups and two sets of the methyl groups to give the one Cp and two methyl resonances observed at -50°C. At higher temperatures the molecule can undergo a trigonal twist about a pseudo-C_3 axis of the octahedron to give a trigonal prismatic transition state where the two mirror planes interconvert the Cp groups and the four methyl groups to give one Cp resonance and one methyl resonance. Twisting through this transition state back to the octahedral structure results in the interconversion of the positions of the methyl groups. Clearly at room temperature the convergence to one methyl peak has not occurred but is being approached at high temperatures.

The energetics of the rearrangement process can easily be calculated since it is a simple, uncoupled, two-site exchange process and the approximate form of the modified Bloch equation can be utilized.[164,165] At the coalescence point the equation is:

$$\frac{1}{\tau} = \frac{\pi \Delta \nu}{\sqrt{2}} \qquad \text{(V-3)}$$


interconverting
Cp
Cp
Me
Me
Me
Me
1
2
3
4
(CO)4
Re
≡

C2: 1 Cp resonance
2 Methyl resonances
(1,4) (2,3)

C2: 1 Cp resonance
2 Methyl resonances
(2,3) (1,4)

2 mirror planes:
1 Cp resonance
1 Methyl resonance

Figure XIX: Intramolecular Nonbond-Rupture Mechanism for $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$.

where τ is the mean preexchange lifetime and $\Delta\nu$ is the difference in frequencies in the absence of exchange. The preexchange lifetime can be related to the free energy of activation by the equation:

$$\frac{1}{\tau} = \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} \qquad \text{(V-4)}$$

where k is the Boltzmann constant, h is Planck's constant and the other symbols have their usual meanings. Thus by combining equation (V-3) and (V-4), an expression for $\Delta G^{\ddagger}$ can be obtained. The coalescence temperature, T_c, in the present case was approximated to be around 35 ± 10°C, the values of $\Delta\nu$ were obtained from Figure XVII and are approximately 550 Hz in CH_2Cl_2 and 780 Hz in toluene. Based on these numbers the $\Delta G^{\ddagger}$ values are 13.7 ± .4 kcal/mole in CH_2Cl_2 and 13.5 ± .5 kcal/mole in toluene. The $\Delta G^{\ddagger}$ values are not very different even though the chemical shift difference, $\Delta\nu$, between the two solvents is significant. The effect of errors in T_c and rate constants on $\Delta G^{\ddagger}$ have been discussed by Kost *et al.*[166] and the insensitivity of the $\Delta G^{\ddagger}$ value is not surprising.

The $\Delta G^{\ddagger}$ values obtained are similar to those found for the tin and transition metal analogues in cases where the coalescence temperature is in approximately the same region. For instance the $\Delta G^{\ddagger}$ value of $Sn(acac)_2F_2$ is 13.3 kcal/mole at T_c = 28°C[160] and the $\Delta G^{\ddagger}$ value of

$Ti(acac)_2(OCH_2CHMe_2)_2$ is 15.61 kcal/mole at T_c = 19°C.[100]

Determining trends in $\Delta G^{\ddagger}$ values can be tenuous since a great deal depends on the system chosen for study. Bickley and Serpone have examined the rates and energetics of the rearrangement process of a number of $Ti(\beta\text{-diketonate})_2X_2$ compounds and have stated that these parameters are not significantly dependent on the substituents of the acetylacetonate ring.[167] It seemed from a study of $Sn(acac)_2X_2$ compounds that varying the X group however did lead to differences in stereochemical lability. For example, the $\Delta G^{\ddagger}$ values of $Sn(acac)_2Cl_2$, $Sn(acac)_2PhCl$ and $Sn(acac)_2Ph_2$ are 15.3,[160] 12.1 [99] and 7.6 [99] kcal/mole respectively. On the other hand, the results of an investigation of dialkoxybis(β-diketonate)titanium(IV) complexes of the type $Ti(\beta\text{-diketonate})_2(OR)_2$ were not so straightforward.[100] When the alkoxy group was OCH_2CHMe_2, then there was very little difference between $Ti(acac)_2(OCH_2CHMe_2)_2$, $\Delta G^{\ddagger}$= 15.61 kcal/mole, and $Ti(dipivaloylmethanate)_2(OCH_2CHMe_2)_2$, $\Delta G^{\ddagger}$= 16.01 kcal/mole. However when the alkoxy group was $OCMe_2Ph$, then there was a significant variation between $Ti(acac)_2(OCMe_2Ph)_2$, $\Delta G^{\ddagger}$= 17.99 kcal/mole, and $Ti(dipivaloylmethanate)_2(OCMe_2Ph)_2$, $\Delta G^{\ddagger}$= 20.57 kcal/mole. The size of the alkoxy group is seemingly controlling the energetics for rearrangement.

Changing the metal centre also affects the rate of rearrangement. The compounds $M(acac)_2X_2$ where M = Zr, Hf and X = Cl, Br are still fluxional down to -130°C[139] whereas the limiting spectra of the titanium analogues could be reached.[159]

It is not possible at the present time to determine the effect of variation in the ligands surrounding the uranium centre on the rate of rearrangement. The ^1H NMR spectrum of the unsymmetrical compound $Cp_2U[cis\text{-}(OCMe)\text{-}(OCCHMe_2)Re(CO)_4]_2$ at ambient temperature was rather featureless, showing only a few small peaks around TMS and 5 ppm above it. The variable temperature NMR experiment was carried out and predictably for a system containing a paramagnetic centre, an asymmetric metalla-β-diketonate ligand and a diasteriotopic isopropyl group, a large number of peaks grew in from the baseline. The analysis of these results was not attempted because of their complexity. However should further ligand changes result in very fast fluxional processes, a study of the system can be aided by the presence of the uranium ion.

The paramagnetic uranium centre permits the measurement of rapid processes because it effectively increases the chemical shift difference between exchanging sites thereby increasing the time resolution of the NMR experiment. The fast exchange of bridge and terminal hydrogen atoms in $Cp_3U(BH_4)$ has been studied using the advantages offered by the paramagnetic uranium.[168] The $\Delta G^{\ddagger}$ value determined was 5.0 ± .6 kcal/mole. Similarly the very fast rearrangement of the methyl groups of U(acac)$_4$ between two different environments in the coordination polyhderon was investigated and shown to proceed with a $\Delta G^{\ddagger}$ value of 5.43 ± .04 kcal/mole.[161]

The ^{13}C NMR data for $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ was also consistent with the cis structural form of the complex. The decoupled and off-resonance spectra at -50°C are shown in Figure XX. They are in agreement with a static structure containing two Cp rings cis to each other and two chelating metalla-acac ligands occupying the remaining positions of an octahedron. The four carbonyls in one metalla-acac ligand are equivalent to the four in the other ligand but in each set they are all inequivalent, hence the appearance of four carbonyl resonances at 196.7, 187.9, 183.1 and 166.0 ppm from TMS. There is one resonance for the carbons of the cyclopentadienyl rings at 165.3 ppm and two acyl carbon and methyl carbon peaks at 341.4 and 294.3 ppm and 86.7 and 83.0 ppm respectively.

The positions of the carbonyl resonances are very similar to other metalla-acetylacetonate complexes. A short list of metalla-acac compounds is given in Table XXI. The chemical shifts for the methyl and one of the acyl carbons of the uranium complex have been shifted downfield a significant amount. It is expected that these carbons would be affected by the paramagnetic uranium centre,

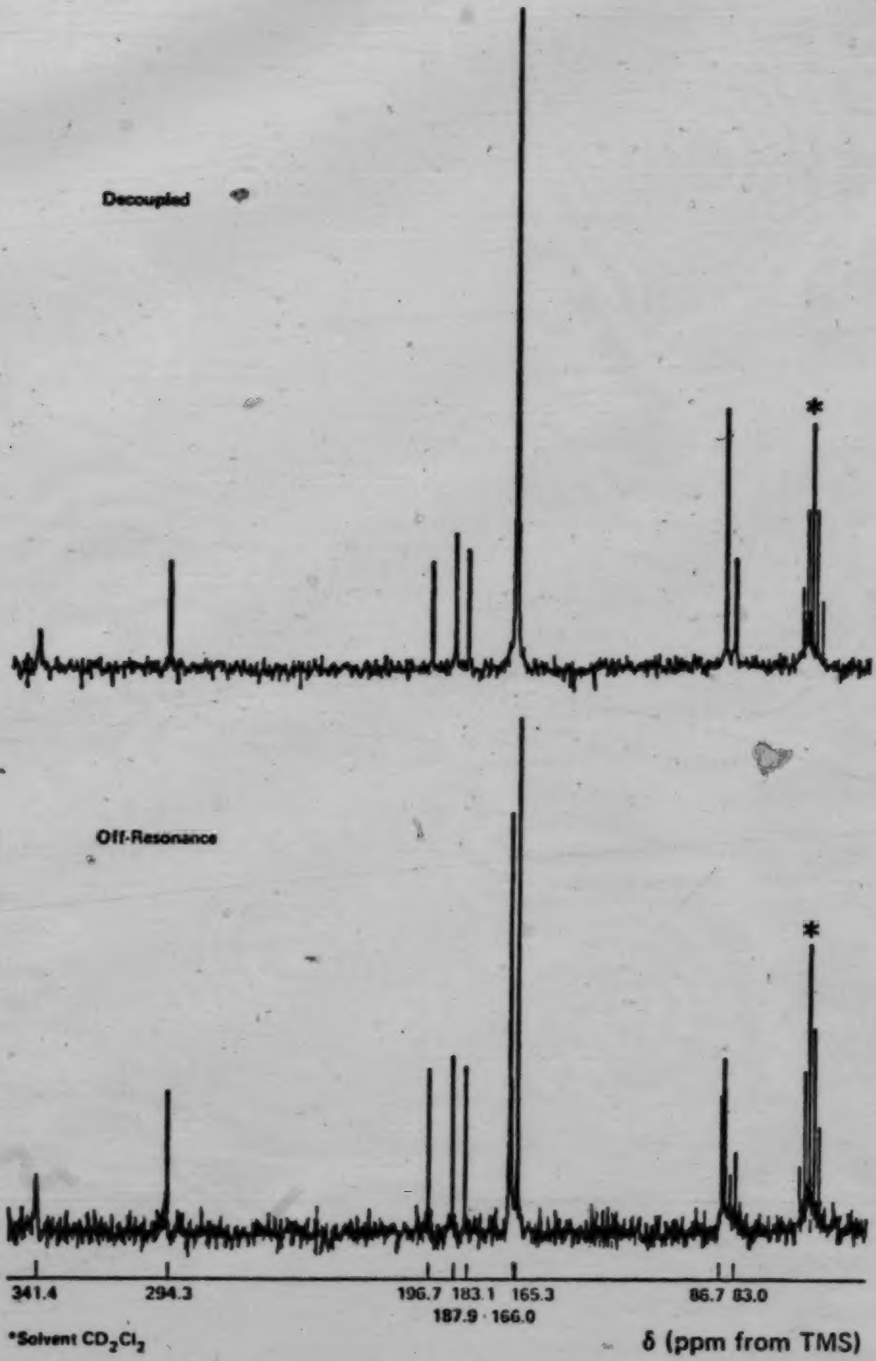


Figure XX: ^{13}C NMR Spectra of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ at −50°C.

Table XXI: ^{13}C NMR Chemical Shift Data for Metalla-Acetylacetonate Derivatives.[a,b]

	CH_3	Acyl	Carbonyl	Other
acetylacetone[c]	24.7	191.9		100.4
cis-$(CO)_4Re(MeCO)_2H$	53.5	297.9	188.0,191.1	
[cis-$(CO)_4Re(MeCO)_2]BF_2$	53.9	314.0	185.6,189.7	
[cis-$(CO)_4Re(MeCO)_2]_3Al$	58.3	301	189.9,191.5	
Cp_2U[cis-$(OCMe)_2Re(CO)_4]_2$	86.7	341.3	196.7,187.9	165.3(Cp)
	83.0	294.3	183.1,166.0	

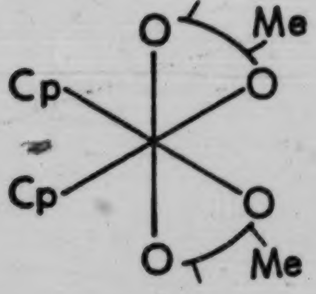
[a] In ppm from TMS.

[b] All compounds except for U-complex from ref. 169.

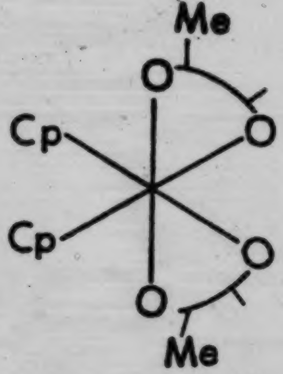
[c] Chemical shifts of the enol tautomer.

whereas the terminal carbonyl carbons are less sensitive.

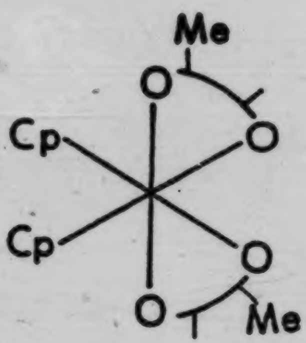
The ^{13}C NMR data of the uranium complexes can be quite useful in determining the number of isomeric forms present in solution. For the unsymmetrical compound three cis isomers are possible as diagrammed below. The number of Cp resonances expected are in parantheses. It should be possible to determine the presence of these isomers by monitoring the number of Cp resonances. In addition the coalescence pattern of these resonances could give insight into the detailed mechanism of the rearrangement in the $Cp_2U(chelate)_2$ type complexes.



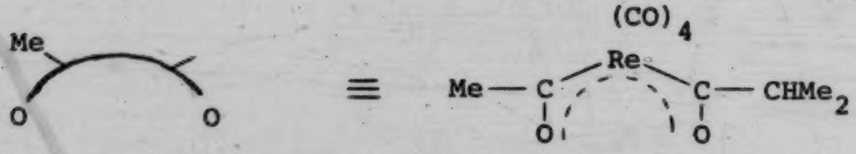
10a
(1)



10b
(1)



10c
(2)



Such a study was done on $Cp_2U[cis\text{-}(OCMe)(OCCHMe_2)\text{-}Re(CO)_4]_2$ but unfortunately there was not enough sample present to conclusively assign the small peaks observed.

Nevertheless the ^{13}C NMR spectrum should be easier to analyze than the ^{1}H NMR spectrum mentioned previously.

All the spectroscopic data collected suggest that $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$ has a monomeric cis-octahedral structure which undergoes rearrangement processes. However a molecular weight determination of the compound in both dichloromethane and acetylacetone gave a number of exactly half of the expected value (588, acetone, 567 CH_2Cl_2 compared to 1137 for monomer). Conductivity measurements in acetonitrile and dichloromethane suggest that no ionic species are present. This result is not surprising since ions of the form $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]^+$-$[(OCMe)_2Re(CO)_4]^-$ are probably not favoured. No explanation can be offered at this time for the discrepancy in the molecular weight data although it is possible that the molecular weight method used was not suitable for these kinds of compounds.

Conclusions

The reagent $Cp_2U(NEt_2)_2$ underwent a very facile substitution reaction with the bulky metalla-acetylacetonate compound, cis-$(CO)_4Re(MeCO)_2H$, to produce the bis(cyclopentadienyl)uranium(IV) derivative. The similar reaction with the unsymmetrical rhenium-enol, cis-$(CO)_4Re(MeCO)$-$(Me_2CHCO)H$, did not lead to a pure product.

The infrared spectral data of $Cp_2U[cis\text{-}(OCMe)_2$-$Re(CO)_4]_2$ showed bidentate coordination of the rhenium-acac ligands. Thus, the environment of the uranium in the complex can be described as pseudo-six coordinate. The variable temperature ^{1}H NMR data conclusively proved that the compound possessed an octahedral structure containing metalla-acac ligands which were cis to each other thereby placing the cyclopentadienyl groups in a cis-orientation as well. The $\Delta G^{\ddagger}$ values calculated for the compound were similar to other metal acac compounds undergoing fluxional behavior.

The synthesis and characterization of other uranium β-diketonate complexes would be of interest since the paramagnetic uranium centre could facilitate the study of fast rearrangement processes that may result from differing ligand environments.

CHAPTER SIX

DICHLOROBIS(DIALKYLAMIDO)-URANIUM(IV) COMPLEXES

Introduction

At the beginning of the thesis work, the pursuit of a synthetic route to the compound Cp_2UCl_2 was still strong. The reason, as mentioned before, was that Cp_2UCl_2 would have been a very versatile reagent for the formation of derivatives of bis(cyclopentadienyl)uranium(IV). Problems with its formation may be due to the inherent instability of Cp_2UCl_2 or the synthetic method employed. The recent reports of $(Me_5C_5)_2UCl_2$[31] and $(Me_4EtC_5)_2UCl_2$[170] do indicate that the instability of Cp_2UCl_2 may be a result of the small cyclopentadienyl group. However, possibly another synthetic route could be used to the formation of Cp_2UCl_2 other than from the UCl_4 salt and cyclopentadienyl anions.

It was postulated that since the reagent $Cp_2U(NEt_2)_2$ had labile uranium-nitrogen bonds which reacted with cyclopentadiene (see equation (II-6)), a starting material of the type $Cl_2U(NR_2)_2$ could also react with cyclopentadiene as in the following reaction and yield perhaps the desired Cp_2UCl_2 compound.

$$Cl_2U(NR_2)_2 + 2CpH \longrightarrow Cl_2UCp_2 + 2HNR_2 \qquad \text{(VI-1)}$$

As well as providing a route to Cp_2UCl_2, compounds of the type $Cl_2U(NR_2)_2$ would also be extremely useful synthetic molecules since they could undergo metathesis reactions involving the chloro ligands and acid-base or insertion reactions as described in preceding chapters with the amide moieties. A related compound, $Cl_2U[HB(N_2C_3H_3)_3]_2$,[137] has been synthesized. The compound is expected to have reactive chloro ligands, although the (pyrazol-1-yl)borate ligands are not as good leaving groups as the amide groups. The synthetic utility of this compound has not been reported as yet. The preparative use of $(Me_5C_5)_2UCl_2$ has already been demonstrated with the metathetical syntheses of $(Me_5C_5)_2UMe_2$ and $(Me_5C_5)_2U(C_4Ph_4)$.[31] Clearly the $Cl_2U(NR_2)_2$ complexes could also provide a route to novel uranium(IV) compounds.

Results and Discussion

The preparation of a variety of $Cl_2U(NR_2)_2$ species was attempted following the reaction below.

$$MNR_2 + UCl_4 \longrightarrow Cl_2U(NR_2)_2 + 2MCl \qquad (VI\text{-}2)$$

$M = Li \quad NR_2 = NEt_2, N(C_6H_{11})_2, N(SiMe_3)_2$

$M = K \quad NR_2 = N(SiMe_3)_2$

Only the compound $Cl_2U[N(C_6H_{11})_2]_2$ was obtained analytically pure. The products formed in the reactions with the other alkali metal amides were monitored by mass spectrometry.

The preparation of pure $Cl_2U[N(C_6H_{11})_2]_2$ resulted from a synthesis in THF solvent. Removal of THF under vacuum produced a gold solid which was extracted into benzene and filtered. The gold solid obtained was analytically pure. The mass spectrum of this solid is given in Table XXII. Attempts to produce crystalline material were not successful. It appeared that dissolving the gold solid in any solvent resulted in decomposition or rearrangement as the solid and solutions became darker during manipulations. It was postulated that the compound $Cl_2U[N(C_6H_{11})_2]_2$ could be isolated initially, however, attempts to redissolve it caused breakdown to possibly $ClU[N(C_6H_{11})_2]_3$. This assumption was given some support by the observation that the higher the probe temperature of the mass spectrometer, the more $ClU[N(C_6H_{11})_2]_3$ was

Table XXII: Summary of Mass Spectrum of $Cl_2U[N(C_6H_{11})_2]_2$.

m/e	Relative Abundance[a,b] (%)	Assignment
668	68.4	$Cl_2U[N(C_6H_{11})_2]_2^+$
633	2.6	$ClU[N(C_6H_{11})_2]_2^+$
586	7.9	$Cl_2U[N(C_6H_{11})_2NH(C_6H_{11})]^+$
487	100	$Cl_2U[N(C_6H_{11})(C_6H_{10})]^+$
404	27.5	$Cl_2U[N(C_6H_{10})]^+$

[a] Not corrected for ^{13}C.

[b] Temp = 210°C.

observed. It can be reasoned that the low coordination number of the uranium in $Cl_2U[N(C_6H_{11})_2]_2$ might be responsible for the possible disproportionation of the molecule which then leads to its breakdown in solution.

An attempt was then made to stabilize the $Cl_2U[N(C_6H_{11})_2]_2$ molecule by forming the dioxane adduct. The strong coordinating ability of dioxane in this type of compound was already noticed in the isolation of the bis(dioxane) adduct $Cl_2Zr(PhNC_2H_4NPh)\cdot 2$ dioxane.[171] The reaction (VI-2) was repeated in dioxane solvent with a small amount of THF added to facilitate the dissolution of UCl_4 and $LiN(C_6H_{11})_2$. The solution was concentrated and filtered to remove LiCl. The supposed adduct was precipitated out of solution by the addition of pentane. However the exact nature of the adduct was difficult to establish. The mass spectrum exhibited a peak for $Cl_2U[N(C_6H_{11})_2]_2^+$ and also for dioxane but not for the adduct. The NMR spectrum of this compound was not very informative since only very broad peaks centered around TMS were observed. It is possible that other resonances could have been detected if a larger sweep width had been used. Elemental analysis was not done on this compound. The physical properties of the dioxane adduct were slightly different than those of the dioxane free complex. For instance $Cl_2U[N(C_6H_{11})_2]_2$ dissolved quite readily in toluene, but the dioxane adduct was only moderately soluble.

The solution also darkened for the adduct as observed before for the dioxane free form. Thus the problems associated with redissolving the material have apparently not been eliminated by coordinating dioxane to the molecule.

In the hopes of producing a more stable $Cl_2U(NR_2)_2$ compound the amine $HN(SiMe_3)_2$ was considered. This bulky amine has been used before in the isolation of metals in low coordination number environments.[46] Unfortunately the reaction with the lithium salt of bistrimethylsilylamine and UCl_4 in THF produced a solid which had a mass spectrum containing mainly fragments from $ClU[N(SiMe_3)_2]_3^+$. Difficulties with removing lithium chloride from the THF solvents prompted the use of the potassium salt of the above silyl amine. Using this salt resulted in mixtures of the bis and trisamide complexes. Sublimation readily occurred at 110°C but both the bis- and tris-substituted compounds were also present in the mass spectral analysis of the sublimate.

The difficulties in preparation and purification of these $Cl_2U(NR_2)_2$ compounds may indicate that their formation and structure are not as straightforward as first expected. The elucidation of this system awaits further study.

The main interest in these compounds was their hoped for reactivity with cyclopentadiene as outlined in equation (VI-3). The initial reaction of the compound

$$Cl_2U(NR_2)_2 + 2CpH \longrightarrow Cp_2UCl_2 + HNR_2 \qquad (VI-3)$$
$$NR_2 = NEt_2,\ N(C_6H_{11})_2$$

$Cl_2U(NEt_2)_2$, prepared *in situ* from UCl_4 and the lithium diethylamide, with almost two equivalents of cyclopentadiene in THF produced a brown solid whose mass spectrum showed the presence of mainly Cp_3UCl but also a small amount of Cp_2UCl_2. Heating the brown solid in THF solvent resulted in the decomposition of Cp_2UCl_2 since a mass spectrum of the residue revealed only Cp_3UCl as the volatile component. These results were interpreted to mean that the *in situ* preparation of $Cl_2U(NEt_2)_2$ could have produced mainly $ClU(NEt_2)_3$ which then reacted with the cyclopentadiene to form Cp_3UCl. The reaction was then repeated in benzene using $Cl_2U[N(C_6H_{11})_2]_2$ in the base free form. The reaction produced an orange solid which had a mass spectrum containing a mixture of Cp_2UCl_2 and $Cl_2U[N(C_6H_{11})_2]_2$. Although no Cp_3UCl was observed, the base peak of the spectrum was for fragments of $Cl_2U[N(C_6H_{11})_2]_2$. The same reaction was repeated in THF but the main product was Cp_3UCl. Using the dioxane adduct form of $Cl_2U[N(C_6H_{11})_2]_2$ did not meet with any greater success. These reactions were done in a solvent mixture of toluene and a small amount of THF. The THF was necessary because $Cl_2U[N(C_6H_{11})_2]_2$ dioxane adduct is only moderately soluble in toluene and dioxane. The reactions produced yellow solids containing varying amounts of Cp_2UCl_2, Cp_3UCl and $Cl_2U[N(C_6H_{11})_2]_2$. The best result obtained was still less than satisfactory: a solid whose mass spectrum contained mainly Cp_2UCl_2 and a fair amount of $Cl_2U[N(C_6H_{11})_2]_2$. An NMR spectrum of this solid in benzene gave a peak at 6.71 ppm above internal benzene. Although this position is where stopcock grease has resonances, the intensity of the peak plus the fact that very little grease was seen in the mass spectrum suggests that the peak is due to Cp_2UCl_2.

There were two other unrelated experiments done with the expectation of producing Cp_2UCl_2. One experiment involved the reaction of UCl_4 and sodium cyclopentadienide in a solvent mixture of dioxane and THF. A very small amount of green solid precipitated out of solution. The mass spectrum of this solid indicated almost pure Cp_2UCl_2. The mass spectral analysis of the solution indicated almost pure Cp_3UCl. This route is obviously not very viable. Another reaction with $Cp_2U(NEt_2)_2$ and Me_3SiCl also produced a small amount of precipitate. However the mass spectrum of this solid showed only a very small amount of Cp_2UCl_2. The attempts to produce Cp_2UCl_2 were abandoned.

The synthetic utility of $Cl_2U(NR_2)_2$ complexes to produce Cp_2UCl_2 was minimal and one of the reasons for this may be the lowered reactivity of the uranium-nitrogen bond in $Cl_2U[N(C_6H_{11})_2]_2$ coupled with the bulky nature of the amide groups. The reactivity of $Cp_2U(NEt_2)_2$ towards carbon disulphide has been discussed in Chapter III. This and other insertion reactions were very facile. A similar reaction with $Cl_2U[N(C_6H_{11})_2]_2$ and carbon disulphide gave only the starting material back.

A study of the reactivity of the uranium-chlorine bonds was not very favourable either. Reactions of $Cl_2U[N(C_6H_{11})_2]_2$ with sodium acetate and potassium cyanide gave no identifiable product in the former case and starting material in the latter. A reaction with sodium cyclopentadiene did produce $Cp_2U[N(C_6H_{11})_2]_2$ but also other combinations containing the ligands Cl, Cp and $N(C_6H_{11})_2$.

Conclusions

The expected synthetic utility of $Cl_2U[N(C_6H_{11})_2]_2$ and the other $Cl_2U(NR_2)_2$ complexes prepared may have been premature. However the failures may be a result of the amide group or solvent conditions or experimental method. Nevertheless compounds of the type $Cl_2U(NR_2)_2$ could be useful reagents and a study of their synthesis and reactivity would be worthwhile.

CHAPTER SEVEN

EXPERIMENTAL

Solvents and General Techniques

All reactions and operations were performed using Schlenk techniques under a static atmosphere of rigorously purified nitrogen. Commercial nitrogen of 99.99% purity or better was passed through a heated column (90-100°C) containing BASF Cu-based catalyst (R3-11) to remove oxygen and a column of Mallinkrodt Aquasorb, which is P_2O_5 on an inert base, to remove water.

All glassware was heated in an oven to 95°C and then immediately evacuated and filled with nitrogen before any operation.

Solvents were dried by both refluxing and distilling from the appropriate drying agent under an atmosphere of nitrogen (Table XXIII). Pentane and ether were also freeze-thaw degassed before use. A number of solvents were preconditioned before being refluxed and distilled under nitrogen. Pentane was washed with concentrated H_2SO_4 and water and dried over $MgSO_4$. Dichloromethane was washed with concentrated H_2SO_4 and water and dried over $CaSO_4$. Tetrahydrofuran was placed over molecular sieves for 24 hours, then refluxed and distilled from $LiAlH_4$.

A silicon lubricant, Dow Corning High Vacuum Grease, was used on all ground glass joints.

Table XXIII. Drying Agents Used for Solvents

Solvent	Drying Agent
Toluene	Sodium metal
Pentane	Calcium hydride
Diethylether	Calcium hydride
Benzene	Potassium metal
Hexane	Potassium metal
Tetrahydrofuran	Sodium-potassium alloy benzophenone
Dichloromethane	Phosphorus pentoxide
Pyridine	Barium oxide molecular sieves

Physical Measurements

Infrared spectra were recorded in the region 4000-250 cm^{-1} with a Perkin-Elmer 467 grating spectrometer. The complexes were studied as Nujol and Fluorolube mulls between potassium bromide plates. The samples were prepared in a glove-bag filled with purified nitrogen.

Proton magnetic resonance spectra were recorded on the following spectrometers: Perkin-Elmer R-32 (35°C), Varian HA-100 (32°C), Varian HA-100 Digilab (32°C), Varian A-60 (44°C) and Bruker WP-60 (30°C). Carbon-13 NMR data were obtained on a Bruker WP-60 (35°C) spectrometer. Variable temperature spectra were recorded on the Perkin-Elmer, Varian HA-100 Digilab and Bruker WP-60 machines, using sealed NMR tubes. Ambient temperature NMR spectra were obtained using serum-stoppered NMR tubes.

Mass spectra were recorded on an AEI-MS12 mass spectrometer operating at 70 eV and at temperatures just sufficient to record the data. Each sample was sealed in a capillary under nitrogen and admitted into the spectrometer using a direct probe technique.

Analyses and molecular weight determinations were performed by Analytische Laboratorien, Postfach 135, D-5250 Engelskirchen, West Germany on samples sent in glass tubes sealed under vacuum.

Reagents and Preparations, Chapter II

Uranium tetrachloride was purchased from ROC/RIC and used as received. Diethylamine (MC/B), pyrrole (Aldrich) and 2,5-dimethylpyrrole (Aldrich) were dried by distilling from potassium metal. Diphenylamine (MC/B) was sublimed before each reaction. Ethyl 3,4,5-trimethylpyrrole 2-carboxylate was supplied by Professor D. Clive of this department and used as received. N-Butyllithium, 15% hexane solution (MC/B) was filtered prior to use. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich, technical grade) at a temperature of 43°C, freeze-thaw degassed and stored at -40°C before use.

Preparation of $Cp_2U(NEt_2)_2$

A summary of the preparative procedures for the synthesis of $Cp_2U(NEt_2)_2$ has been given in Table I. Two procedures will be outlined below.

THF solvent:

N-BuLi (74.0 ml, 115 mmol) was added dropwise at 0°C to a solution of $HNEt_2$ (13 ml, 126 mmol) in 20 ml of hexane. The solution was stirred for 1.5 h, the solvent was then removed and the resulting white solid was dried under vacuum.

UCl_4 (9.03 g, 23.8 mmol) was dissolved in 60 ml of THF initially at 0°C, then at approximately 50°C. This green solution was added dropwise to a solution of $LiNEt_2$ (7.52 g, 95.1 mmol) in 30 ml of THF at 0°C, with the exclusion of light. The dark-green solution was stirred for 30 h at room temperature. The solvent was removed under vacuum and the resultant $U(NEt_2)_4$ was extracted with 80 ml of pentane and filtered. To this solution, at 0°C, was added a solution of CpH (2.80 ml, 33.8 mmol) in 25 ml of pentane. The dropping funnel was rinsed with another 10 ml of pentane. The reaction mixture was stirred for 2 h at 0°C, followed by 1 h at room temperature. After this point there is no need to exclude light from the reaction mixture. The gold-brown solution was transferred to a jacketed filter, cooled to -78°C for .5 h and the resultant gold flakes were filtered from the solvent. The solid was washed with 20 ml of cold pentane and then dried under vacuum to give a yield of 60.1%.

Et_2O solvent:

N-BuLi (50.5 ml, 125 mmol) was added dropwise at 0°C to a solution of $HNEt_2$ (13 ml, 126 mmol) in 40 ml of hexane. The solution was stirred for 3 h at room temperature, filtered and the resultant white solid was washed with 5 ml of hexane and then dried under vacuum.

UCl_4 (10.48 g, 27.6 mmol) and $LiNEt_2$ (8.79 g, 111 mmol) were placed in a 300 ml flask, which was then wrapped in foil to exclude light. Into the flask was transferred 100 ml of Et_2O under vacuum at liquid N_2 temperature. The reaction mixture was stirred at room temperature for 30 h, filtered and the solvent removed under vacuum. The resulting dark green oil was dissolved in 60 ml of pentane. To this solution, cooled to 0°C was added a solution of CpH (3.3 ml, 39.8 mmol) in 20 ml of pentane. The solution was stirred at room temperature for 7 h in a foil-wrapped flask. The gold-brown solution was then transferred to a jacketed filter, cooled to -78°C for .5 h and the resulting gold flakes were filtered from the solvent. The solid was then washed with 15 ml of pentane and dried under vacuum to give a yield of 78.5%.

The filtrate solutions in the above preparations can be concentrated and cooled to yield more product which however also contains more of the impurity $Cp_3U(NEt_2)$.

$Cp_2U(NEt_2)_2$ will form small amounts of $Cp_3U(NEt_2)$ upon handling and storage, so to remove this impurity, the sample is dissolved in hexane and filtered prior to use. The purity may be ascertained by recording the NMR spectrum.

Preparation of $Cp_2U(NEt_2)(NPh_2)$

$HNPh_2$ (.642 g, 3.79 mmol) was dissolved in 30 ml of hexane and added to a solution of $Cp_2U(NEt_2)_2$ (1.94 g, 3.78 mmol) in 50 ml of hexane at room temperature. There was an immediate colour change from gold-brown to red, but no precipitate was noticed. The reaction mixture was stirred at room temperature for 37 h. Upon concentration of the solution an orange-red precipitate was observed. The solvent was completely removed under vacuum, resulting in an orange-red solid to give a yield of 59.5%. Crystallization was affected from a toluene/hexane solvent mix.

Anal. Calcd for $C_{26}H_{30}N_2U$: C, 51.32; H, 4.97; N, 4.60; U, 39.11. Found: C, 51.13; H, 4.80; N, 4.47; U, 39.42.

Attempted Preparation of $Cp_2U(NC_4H_4)_2$

A mixture of HNC_4H_4 (.60 ml, 8.67 mmol) and 10 ml of hexane was added dropwise at 0°C to a solution of $Cp_2U(NEt_2)_2$ (2.18 g, 4.24 mmol) in 35 ml of hexane. There was an immediate precipitation of a gold-brown solid. The reaction mixture was stirred for 2 h at 0°C and a further 27 h at room temperature. The solution was filtered resulting in a gold-brown solid and a clear pink filtrate. The gold-brown solid, obtained in almost quantitative yield, produced a mass spectrum indicative of a 50/50 mixture of $Cp_2U(NC_4H_4)_2$ and $Cp_3U(NC_4H_4)$.

Attempted Preparation of $Cp_2U(NC_4H_2Me_2)_2$

$NHC_4H_2Me_2$ (.45 ml, 4.42 mmol) was syringed slowly into a solution of $Cp_2U(NEt_2)_2$ (.941 g, 1.84 mmol) in 40 ml of hexane at room temperature. No heat evolution, colour change or precipitation was observed. The solution was stirred for 34 h and then the solvent was removed under vacuum resulting in the formation of a red sticky solid. To this solid was added 15 ml of diethylether resulting in a red solution. Upon cooling, red needle-like crystals were obtained which when dried under vacuum deteriorated to a flaky red solid. The NMR spectrum and mass spectral data indicated that the red solid was a mixture of $Cp_3U(NEt_2)$ and $Cp_2U(NEt_2)(NC_4H_2Me_2)$.

Preparation of $Cp_2U[NC_4Me_3(COOEt)]_2$

A solution of $HNC_4Me_3(COOEt)$ (.239 g, 1.32 mmol) in 3 ml of THF and 10 ml of hexane was syringed slowly into a solution of $Cp_2U(NEt_2)_2$ (.372 g, .73 mmol) in 20 ml of hexane at room temperature. The solution was stirred for 24 h at the end of which time the solution was red-brown with a greenish tinge. The solvent was removed under vacuum and a yellow-brown solid was obtained. To this solid was added 10 ml of pentane and this solution was then stirred for 24 h. The solution was filtered and the green solid obtained was dried under vacuum to give a yield of 48.2% The green solid could be sublimed at 110°C, although the sublimation was not very efficient. Mass spectral data and an NMR spectrum confirmed that the green solid was $Cp_2U[NC_4Me_3(COOEt)]_2$.

Reagents and Preparations, Chapter III

The compound $Cp_2U(NEt_2)_2$ was synthesized and purified according to the procedure outlined above. Carbon disulfide (reagent grade, Anachemia) was refluxed over P_2O_5 and distilled. Dissolved oxygen was displaced by vigorously bubbling nitrogen through the liquid. Carbonyl sulfide (Matheson) was purified of H_2S contaminant by reaction with lead acetate. Carbon dioxide (glass flask assayed, research purity, Airco) was used as received.

Preparation of $Cp_2U(S_2CNEt_2)_2$

Carbon disulfide (2.6 ml, 43.1 mmol) was added to 10 ml of pentane and this solution was added dropwise at room temperature to a solution of $Cp_2U(NEt_2)_2$ (1.84 g, 3.6 mmol) in 30 ml of pentane. After the addition, the dropping funnel was rinsed with 10 ml of pentane and 30 ml of benzene. After 3 hours the colour of the solution was orange-red and there was a slight reddish precipitate. The solution was stirred for an additional 18 h and then filtered to give a red solid, $Cp_2U(S_2CNEt_2)_2$.

Anal. Calcd for $C_{20}H_{30}N_2S_4U$: C, 36.14; H, 4.55; N, 4.21; U, 35.81; mol. wt., 665. Found: C, 35.91; H, 4.40; N, 4.11; U, 35.49; mol. wt., 682 (osmometry in benzene).

Preparation of $Cp_2U(OSCNEt_2)_2$

$Cp_2U(NEt_2)_2$ (.489 g, 9.54 mmol) was dissolved in 12 ml of pentane, then placed in a liquid N_2 bath. Carbonyl sulphide (.218 g, 3.64 mmol) was transferred to the frozen bulb by trap-to-trap distillation. The bulb was allowed to warm to room temperature during which time a brown precipitate formed, the reaction solution was stirred for a further two hours at room temperature. The excess COS and pentane were removed under vacuum and the resulting gold-brown solid was collected.

Anal. Calcd for $C_{20}H_{30}N_2O_2S_2U$: C, 37.97; H, 4.78; N, 4.43; S, 10.14; U, 37.63; mol. wt., 634. Found: C, 37.69; H, 4.66; N, 4.33; S, 10.91; U, 37.44; mol. wt., 664 (osmometry in benzene).

Preparation of $Cp_2U(O_2CNEt_2)_2$

$Cp_2U(NEt_2)_2$ (1.83 g, 3.57 mmol) was dissolved in 50 ml of pentane and cooled to -78°C. Carbon dioxide (8.4 mmol) was condensed onto this solution. The flask was then allowed to warm to room temperature and the solution was stirred for an additional 5 h. The dark green reaction mixture was filtered to give a dark green product. The material was crystallized from a toluene/ hexane mixture to give analytically pure $Cp_2U(O_2CNEt_2)_2$.

Anal. Calcd for $C_{20}H_{30}O_4N_2U$: C, 40.00; H, 5.04; O, 10.66; N, 4.66; mol. wt., 600. Found: C, 39.74, H, 4.91; O, 10.44; N, 4.70; mol. wt., 7200, 4900 (osmometry in benzene), 1790 (osmometry in CH_2Cl_2).

Reagents and Preparations, Chapter IV

The compound $Cp_2U(NEt_2)_2$ was prepared as described above. Benzoic acid (Fisher), previously recrystallized, was pumped to dryness under vacuum. Trimethylacetic acid (pivalic acid) (Aldrich) was pumped to dryness under vacuum, however, this was only done for a short period of time as the compound sublimes at room temperature. Concentrated glacial acetic acid (Fisher) was used as received. Thiobenzoic acid (Aldrich) was dried by adding $MgSO_4$ to a solution of the acid dissolved in hexane. The slurry was stirred, filtered and the solvent removed under vacuum. The yellow liquid was then used without further purification. Thioacetic acid (Aldrich) was stirred over $MgSO_4$, filtered and distilled resulting in a yellow liquid.

Preparation of $Cp_2U(O_2CMe)_2$

$Cp_2U(NEt_2)_2$ (2.26 g, 4.42 mmol) was dissolved in 70 ml of hexane, stirred and filtered. To this solution at 0°C was added a solution of MeCOOH (.50 ml, 8.74 mmol) in 30 ml of hexane. There was an immediate colour change from gold-brown to green-brown along with the observation of a faint cloudiness above the solution. As the addition proceeded a green precipitate was formed. After stirring at room temperature for 18.5 h, the lime green supernatant liquid was decanted and the remaining pale green solid was dried under vacuum to give a yield of 68.4%. This solid is insoluble in benzene, acetone, dichloromethane, tetrahydrofuran, acetonitrile and nitromethane, but very soluble in pyridine.

Anal. Calcd for $C_{14}H_{16}O_4U$: C, 34.58; H, 3.32; O, 13.16; U, 48.95. Found: C, 33.81; H, 3.38; O, 12.75; U, 48.50. Because of low solubility, molecular weight data could not be obtained.

Preparation of $Cp_2U(OSCMe)_2$

$Cp_2U(NEt_2)_2$ (1.90 g, 3.71 mmol) was dissolved in 50 ml of hexane, stirred and filtered. To this solution at 0°C was added through a transfer tube a solution of MeCOSH (.510 g, 6.70 mmol) in 15 ml of hexane. The flask and transfer tube were washed with another 20 ml of hexane. There was an immediate precipitation of a green solid along with faint cloudiness above the solution. The slurry was stirred for 10 h at room temperature. The green supernatant solution was decanted and the resulting green precipitate was dried under vacuum to give a yield of 60.1%. The compound sublimed at 100°C under a mercury diffusion pump vacuum, although the sublimation was not very efficient.

Anal. Calcd for $C_{14}H_{16}O_2S_2U$: C, 32.43; H, 3.11; O, 6.17; S, 12.37; U, 45.91. Found: C, 32.17; H, 3.21; O, 5.98; S, 12.14; U, 46.20.

Molecular weight data is not available since the compound decomposed at the temperature at which measurements were made.

Preparation of $Cp_2U(OSCPh)_2$

$Cp_2U(NEt_2)_2$ (2.20 g, 4.29 mmol) was dissolved in 50 ml of hexane, stirred and filtered. To this solution at 0°C was added through a transfer tube a solution of PhCOSH (1.28 g, 9.24 mmol) in 10 ml of hexane. There was an immediate precipitation of a red solid along with the formation of a white cloudiness above the solution. The flask and transfer tube were rinsed with another 15 ml of hexane after which the reaction mixture was stirred for 10 h at room temperature. The red supernatant solution was decanted and the red solid remaining in the flask was dried *in vacuo* to give a yield of 58.3%.

The red solid is soluble in benzene, toluene, CS_2 and dichloromethane.

Anal. Calcd for $C_{24}H_{20}O_2S_2U$: C, 44.86; H, 3.14; O, 4.98; S, 9.98; U, 37.04; mol. wt., 643. Found: C, 44.65; H, 3.26; O, 5.15; S, 10.03; U, 36.86; mol. wt., 619 (osmometry in CH_2Cl_2).

Preparation of $Cp_2U(O_2CPh)_2$

To a solution of $Cp_2U(NEt_2)_2$ (1.43 g, 2.79 mmol) dissolved in 40 ml of toluene and cooled to 0°C was added, through a dropping funnel, a solution of $PhCO_2H$ (.68 g, 5.57 mmol) in 20 ml of toluene. There was immediate precipitation of a green solid in the reaction mixture which was then stirred at room temperature for 63 h. The solution was filtered, the green solid washed with 20 ml of toluene and then collected to give a yield of 51.4 %. The yield may be low due to some decomposition of the initial starting reagent which had a darker colour than normal.

The green solid is soluble in pyridine, slightly soluble in THF and insoluble in benzene, toluene and hexane.

Anal. Calcd for $C_{24}H_{20}O_4U$: C, 47.22; H, 3.30; O, 10.48. Found: C, 47.07; H, 3.41; O, 5.34 (10.68).

The oxygen analysis is approximately 50% of the expected value, a result which also occured for the compound $Cp_2U(O_2CCMe_3)_2$. The analytical laboratory mentioned that for procedural reasons in similar organometallic compounds sometimes only one C-bonded oxygen atom is determined.

Based on mass spectral results and the carbon, hydrogen data, it is assumed that the benzoate complex was formed.

Preparation of $Cp_2U(O_2CCMe_3)_2$

$Cp_2U(NEt_2)_2$ (2.74 g, 5.35 mmol) was dissolved in 20 ml of hexane, stirred and filtered. To this solution at 0°C was added, through a dropping funnel, a solution of Me_3CCO_2H (.983 g, 9.63 mmol) in 30 ml of hexane. The funnel was rinsed with a further 10 ml of hexane. A very small amount of green precipitate was observed. The opaque dark green reaction mixture was stirred at room temperature for 17 h. The solution was concentrated to a quarter of the original volume and the supernatant solution was decanted. The remaining green solid was dried *in vacuo* to give a yield of 68%. The NMR spectrum of this green solid indicated pure $Cp_2U(O_2CCMe_3)_2$. This compound can be crystallized from a concentrated solution of hexane. Crystals from this type of crystallization were analyzed.

Anal. Calcd for $C_{20}H_{28}O_4U$: C, 42.11; H, 4.95; O, 11.22; mol. wt., 571. Found: C, 41.95; H, 5.10; O, 5.71; mol. wt., 1151 (osmometry in benzene).

Again the oxygen analysis is low by half. The same explanation about the method of analysis applies to this compound as for the benzoate complex.

Attempted Preparation of $Cp_2U(NEt_2)(O_2CCMe_3)$

$Cp_2U(NEt_2)_2$ (4.12 g, 8.03 mmol) was dissolved in 60 ml of hexane, stirred and filtered. To this solution at room temperature was added through a transfer tube a solution of Me_3CCO_2H (.813 g, 7.96 mmol) in 30 ml of hexane. The flask and transfer tube were rinsed with another 20 ml of hexane. The reaction mixture was stirred at room temperature for 22 h. A 5 ml aliquot of the solution was transferred to a small flask where the solvent was removed under vacuum, resulting in a gold-brown oily solid. NMR analysis of this oily solid indicated that a mixture of $Cp_2U(NEt_2)(O_2CCMe_3)$, $Cp_2U(O_2CCMe_3)_2$ and $Cp_2U(NEt_2)_2$ was present.

Reagents and Preparations, Chapter V

The compounds cis-$(CO)_4Re(MeCO)_2H$ and cis-$(CO)_4Re(MeCO)(Me_2HCCO)H$ were provided by Professor C.M. Lukehart of Vanderbilt University. The acid, cis-$(CO)_4Re(MeCO)(Me_2HCCO)H$, was used as received. The acid, cis-$(CO)_4Re(MeCO)_2H$, was recrystallized from hexane. The compound, $Cp_2U(NEt_2)_2$, was prepared as described above.

Preparation of $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$

To a solution of $Cp_2U(NEt_2)_2$ (.140 g, .273 mmol) in 15 ml of hexane at 0°C was added dropwise a slurry of cis-$(CO)_4Re(MeCO)_2H$ (.199 g, .516 mmol) in 20 ml of hexane. The brown solution became orange coloured and by the end of the addition of the rhenium-enol, a yellow precipitate was apparent. The solution was stirred for 2 h at 0°C, concentrated down to approximately 20 ml, then cooled to -40°C for .5 h and quickly filtered yielding a yellow solid which was pumped to dryness under vacuum to give a yield of 45.8%. Although the reported yield is low in fact an almost quantitative amount of solid was obtained but due to its fine powdery nature a quantitative transfer was difficult. The compound is soluble in dichloromethane, acetone and toluene, moderately soluble in carbon disulphide and benzene and slightly soluble in acetonitrile.

Anal. Calcd for $C_{26}H_{22}O_{12}URe_2$: C, 27.50; H, 1.95; O, 16.89; U, 20.94; mol. wt., 1137. Found: C, 27.37; H, 2.02; O, 16.62; U, 20.66; mol. wt., 567 (osmometry in CH_2Cl_2) and C, 27.66; H, 2.09; mol. wt., 588 (osmometry in acetone).

Preparation of $Cp_2U[cis\text{-}(OCMe)(OCCHMe_2)Re(CO)_4]_2$

To a solution of $Cp_2U(NEt_2)_2$ (.388 g, .756 mmol) in 25 ml of hexane at 0°C was added dropwise a slurry of cis-$(CO)_4Re[(MeCO)(Me_2HCCO)_2]H$ (.611 g, 1.48 mmol) in 40 ml of hexane. The dropping funnel was rinsed with 10 ml of hexane. The brown solution turned a murky yellow in appearance. The solution was stirred at 0°C for 2 h and 18.5 h at room temperature, however there was no further colour change. The solvent was removed under vacuum resulting in a yellow-brown solid. The ^1H NMR spectrum of this solid indicated that a pure compound had not been obtained.

Attempts to crystallize the compound from various solvent mixtures (toluene/hexane, CH_2Cl_2, pentane) all met with failure.

Reagents and Preparations, Chapter VI

A number of reactions were discussed in Chapter VI but only the one successful preparation will be described.

Dicyclohexylamine (Eastman Organic Chemicals) was distilled from potassium metal and freeze-thaw degassed prior to use. N-butyllithium, 15% hexane solution (MC/B) was filtered prior to use. Uranium tetrachloride was prepared following the procedure of Hermann and Suttle[172] except that the green UCl_4 formed was filtered and washed with carbon tetrachloride to remove the trichloroacryloyl chloride.

Preparation of $Cl_2U[N(C_6H_{11})_2]_2$

N-BuLi (36.5 ml, 61.0 mmol) was added dropwise at 0°C to a solution of $HN(C_6H_{11})_2$ (12.5 ml, 62.9 mmol) in 10 ml of hexane. The dropping funnel was rinsed with a futher 20 ml of hexane and the solution was stirred for 12 h at room temperature. The solution was allowed to settle and the white solid was washed with 2 x 30 ml of hexane to remove excess $HN(C_6H_{11})_2$. The solid was dried under vacuum. To a solution of UCl_4 (10.35 g, 27.2 mmol) in 70 ml of THF at 0°C was added dropwise a solution of

$LiN(C_6H_{11})_2$ (10.10 g, 53.9 mmol) in 50 ml of THF. The dropping funnel was rinsed with another 35 ml of THF. The dark green reaction mixture was stirred for 8 h, then the solvent was removed and the resulting gold solid dried under vacuum. The solid was extracted into 110 ml of benzene, filtered, the solvent removed and the gold solid dried under vacuum to give a yield of 65.9%.

Anal. Calcd for $C_{24}H_{44}N_2Cl_2U$: C, 43.05; H, 6.62; N, 4.18. Found: C, 42.80; H, 6.65; N, 4.04.

REFERENCES

1. U. Müller-Westerhoff and A.D. Streitwieser, J. Am. Chem. Soc., 90, 7364 (1968).
2. L. T. Reynolds and G. Wilkinson, J. Inorg. Nucl. Chem., 2, 246 (1956).
3. E. O. Fischer and Y. Hristidu, Z. Naturforsch. B, 17, 275 (1962).
4. E. O. Fischer and A. Treiber, Z. Naturforsch. B, 17, 276 (1962).
5. R. Von Ammon, B. Kanellakopulos, and R. D. Fischer, Chem. Phys. Lett., 2, 513 (1968).
6. T. H. Siddall, W. E. Stewart, and D. G. Karraker, Chem. Phys. Lett., 3, 498 (1969).
7. R. Von Ammon, B. Kanellakopulos, and R. D. Fischer, Chem. Phys. Lett., 4, 553 (1970).
8. M. L. Anderson and L. R. Crisler, J. Organomet. Chem., 17, 345 (1969).
9. A. Streitwieser, U. Müller-Westerhoff, G. Sonnichsen, F. Mares, D. G. Morrell, K. O. Hodgson, and C. A. Harmon, J. Am. Chem. Soc., 95, 8644 (1973).
10. T. J. Marks, A. M. Seyam, and J. R. Kolb, J. Am. Chem. Soc., 95, 5529 (1973).
11. A. E. Gebala and M. Tsutsui, J. Am. Chem. Soc., 95, 91 (1973).
12. R. Von Ammon, R. D. Fischer, and B. Kanellakopulos, Chem. Ber., 105, 45 (1972).

13. a) Lanthanide and Actinide Annual Surveys:

F. Calderazzo, J. Organomet. Chem., 53, 173 (1973).

F. Calderazzo, J. Organomet. Chem., 79, 175 (1974).

T. J. Marks, J. Organomet. Chem., 79, 181 (1974).

T. J. Marks, J. Organomet. Chem., 95, 301 (1975).

T. J. Marks, J. Organomet. Chem., 119, 229 (1976).

T. J. Marks, J. Organomet. Chem., 138, 157 (1977).

b) B. Kanellakopulos and K. W. Bagnall, MTP Int. Rev. Sci., Inorg. Chem., Ser. One, 7, 299 (1972).

c) R. G. Hayes and J. L. Thomas, Organomet. Chem. Rev., Sect. A, 7, 1 (1971).

d) E. Cernia and A. Mazzei, Inorg. Chim. Acta, 10, 239 (1974).

e) M. Tsutsui, N. Ely, and R. Dubois, Acc. Chem. Res., 9, 217 (1976).

f) T. J. Marks, Acc. Chem. Res., 9, 223 (1976).

14. C. A. Harmon, D. P. Bauer, S. R. Berryhill, K. Hagiwara, and A. Streitwieser, Inorg. Chem., 16, 2143 (1977).

15. C. B. Grant and A. Streitwieser, J. Am. Chem. Soc., 100, 2433 (1978).

16. F. R. Fronczek, G. W. Halstead, and K. N. Raymond, J. Am. Chem. Soc., 99, 1769 (1977).

17. V. K. Vasil'ev, V. N. Sokolov, and G. P. Kondratenkov, J. Organomet. Chem., 142, C7 (1977).

18. J. Goffart, B. Gilbert, and G. Duyckaerts, Inorg. Nucl. Chem. Lett., 13, 189 (1977).

19. J. Goffart and G. Duyckaerts, Inorg. Nucl. Chem. Lett., 14, 15 (1978).

20. K. W. Bagnall, J. Edwards, and A. C. Tempest, J. Chem. Soc., Dalton Trans., 295 (1978).

21. E. R. Sigurdson and G. Wilkinson, J. Chem. Soc., Dalton Trans., 812 (1977).

22. K.-H. Thiele, R. Opitz, and E. Köhler, Z. Anorg. Allg. Chem., 435, 45 (1977).

23. P. Zanella, S. Faleschini, L. Doretti, and G. Faroglia, J. Organomet. Chem., 26, 353 (1971).

24. B. Kanellakopulos, C. Aderhold, and E. Dornberger, J. Organomet. Chem., 66, 447 (1974).

25. a) G. Chandra and M. F. Lappert, J. Chem. Soc. A, 1940 (1968).

b) G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, J. Chem. Soc. A, 2550 (1970).

26. R. G. Jones, G. Karmas, G. A. Martin Jr., and H. Gilman, J. Am. Chem. Soc., 78, 4285 (1956).

27. G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmerman, Angew. Chem., Int. Ed. Engl., 5, 151 (1966).

28. D. C. Bradley and M. H. Gitlitz, J. Chem. Soc. A, 980 (1969).

29. J. D. Jamerson and J. Takats, J. Organomet. Chem., 78, C23 (1974).

30. C. A. Secaur, V. W. Day, R. D. Ernst, W. J. Kennelly, and T. J. Marks, J. Am. Chem. Soc., 98, 3713 (1976).

31. J. M. Manriquez, P. J. Fagan, and T. J. Marks, J. Am. Chem. Soc., 100, 3939 (1978).

32. P. Zanella, G. De Paoli, G. Bombieri, G. Zanotti, and R. Rossi, J. Organomet. Chem., 142, C21 (1977).

33. R. E. Cramer, R. B. Maynard, and J. W. Gilje, Abstracts of the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978, INOR 69.

34. A. M. Seyam and G. A. Eddein, Inorg. Nucl. Chem. Lett., 13, 115 (1977).

35. E. C. Baker, G. W. Halstead, and K. N. Raymond, Struct. Bonding (Berlin), 25, 23 (1976).

36. I. Fragala, E. Ciliberto, R. D. Fischer, G. R. Sienel, and P. Zanella, J. Organomet. Chem., 120, C9 (1976).

37. I. Fragala, G. Condorelli, P. Zanella, and E. Tondello, J. Organomet. Chem., 122, 357 (1976).

38. J. P. Clark and J. C. Green, J. Chem. Soc., Dalton Trans., 505 (1977).

39. J. D. Jamerson, Ph.D. Thesis, University of Alberta, Edmonton, Alberta, 1974.

40. U. Schröer, H-J. Albert, and W. P. Neumann, J. Organomet. Chem., 102, 291 (1975).

41. D. L. Tomaja and J. J. Zuckerman, Syn. React. Inorg. Met. -Org. Chem., 6, 323 (1976).

42. J. L. Calderon, F. A. Cotton, and J. Takats, J. Am. Chem. Soc., 93, 3587 (1971).

43. F. W. Siegert and H. J. De Liefde Meijer, J. Organomet. Chem., 20, 141 (1969).

44. V. I. Kulishov, E. M. Brainina, N. G. Bokiy, and Yu. T. Struchkov, J. Organomet. Chem., 36, 333 (1972).

45. E. C. Baker, K. N. Raymond, T. J. Marks, and W. A. Wachter, J. Am. Chem. Soc., 96, 7586 (1974).

46. D. C. Braley and M. H. Chisholm, Acc. Chem. Res., 9, 273 (1976).

47. D. C. Bradley, Adv. Inorg. Chem. Radiochem., 15, 259 (1972).

48. A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, J. Organomet. Chem., 23, 165 (1970).

49. J. G. Reynolds, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, Inorg. Chem., 15, 2498 (1976).

50. J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, Inorg. Chem., 16, 1090 (1977).

51. J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, Inorg. Chem., 16, 599 (1977).

52. J. G. Reynolds, A. Zalkin, D. H. Templeton, and N. M. Edelstein, Inorg. Chem., 16, 1858 (1977).

53. M. H. Chisholm, F. A. Cotton, and M. W. Extine, Inorg. Chem., 17, 1329 (1978).

54. G. W. Watt and K. F. Gadd, Inorg. Nucl. Chem. Lett., 9, 203 (1973).

55. J. G. Reynolds and N. M. Edelstein, private communication.

56. M. F. Lappert and A. R. Sanger, J. Chem. Soc. A, 1314 (1971).

57. T. J. Marks and J. R. Kolb, J. Organomet. Chem., 82, C35 (1974).

58. R. D. Fischer in "Chemical Applications of NMR in Paramagnetic Molecules", G. N. La Mar, W. D. Horrocks Jr., and R. H. Holm, Ed., Academic Press, New York, N.Y., 1973, Chapter 13.

59. J. G. Reynolds and N. M. Edelstein, Inorg. Chem., 16, 2822 (1977).

60. V. T. Aleksanyan and B. V. Lokshin, J. Organomet. Chem., 131, 131 (1977).

61. H. P. Fritz, Adv. Organomet. Chem., 1, 239 (1964).

62. M. Tsutsui, N. Ely, and A. Gebala, Inorg. Chem., 14, 78 (1975).

63. Von K. Issleib and G. Batz, Z. Anorg. Allg. Chem., 369, 83 (1969).

64. J. Willemse, J. A. Cras, J. J. Steggerda, and C. P. Keijzers, Struct. Bonding (Berlin), 28, 83 (1976).

65. K. W. Bagnall and E. Yanir, J. Inorg. Nucl. Chem., 36, 777 (1974).

66. K. W. Bagnall, D. Brown, and D. G. Holah, J. Chem. Soc. A, 1149 (1968).

67. a) M. H. Chisholm and M. W. Extine, J. Am. Chem. Soc., 99, 792 (1977).

b) C. G. Pierpont, R. C. Dickinson, and B. J. McCormick, Inorg. Chem., 13, 1674 (1974).

c) J. G. Leipoldt and P. Coppens, Inorg. Chem., 12, 2269 (1973).

68. H. Nakajima and T. Tanaka, J. Inorg. Nucl. Chem., 39, 991 (1977) and references therein.

69. T. A. George, K. Jones, and M. F. Lappert, J. Chem. Soc., 2157 (1965).

70. R. F. Dalton and K. Jones, J. Chem. Soc. A, 590 (1970).

71. K. W. Given, B. W. Mattson, G. L. Miessler, and L. H. Pignolet, J. Inorg. Nucl. Chem., 39, 1309 (1977).

72. C. S. Harreld and E. O. Schlemper, Acta Crystallogr., Sect. B, 27, 1964 (1971).

73. A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, J. Chem. Soc., Chem. Commun., 476 (1976).

74. O. A. Ileperuma and R. D. Feltham, Inorg. Chem., 14, 3042 (1975).

75. P. Jennische and R. Hesse, Acta Chem. Scand., 25, 423 (1971).

76. H. P. Klug, Acta Cryst., 21, 536 (1966).

77. F. Calderazzo, G. Dell'Amico, M. Pasquali, and G. Perego, Inorg. Chem., 17, 474 (1978).

78. D. D. Bradley and M. H. Gitlitz, J. Chem. Soc. A, 1152 (1969).

79. T. N. Srivastava and V. Kumar, J. Organomet. Chem., 107, 55 (1976).

80. T. N. Srivastava, V. Kumar, and R. B. Rastogi, J. Inorg. Nucl. Chem., 40, 399 (1978).

81. R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini, and E. Tondello, Inorg. Chem., 9, 2116 (1970).

82. D. F. Lewis and R. C. Fay, J. Am. Chem. Soc., 96, 3843 (1974).

83. M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, J. Chem. Soc., Chem. Commun., 743 (1970).

84. A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark, and S. H. Strauss, Inorg. Chem., 13, 886 (1974).

85. E. C. Alyea, B. S. Ramaswamy, A. N. Bhat, and R. C. Fay, Inorg. Nucl. Chem. Lett., 9, 399 (1973).

86. W. L. Steffen, S. L. Hawthorne, and R. C. Fay, J. Am. Chem. Soc., 98, 6757 (1976).

87. J. Ahmed and J. A. Ibers, Inorg. Chem., 16, 935 (1977).

88. H. Nakajima, T. Tanaka, H. Kobayaski, and I. Tsujikawa, Inorg. Nucl. Chem. Lett., 12, 689 (1976).

89. N. Sonoda and T. Tanaka, Inorg. Chim. Acta, 12, 261 (1975).

90. a) M. H. Chisholm and M. Extine, J. Am. Chem. Soc., 97, 1623 (1975).
    b) M. H. Chisholm and M. W. Extine, J. Am. Chem. Soc., 99, 782 (1977).

91. R. Choukroun and D. Gervais, Synth. React. Inorg. Met.-Org. Chem., 8, 137 (1978).

92. D. Brown, D. G. Holah, C. E. F. Richard, and P. T. Moseley, U.K. At. Energy Authority Report, R-6907 (1971).

93. F. Calderazzo, G. Dell'Amico, R. Netti, and M. Pasquali, Inorg. Chem., 17, 471 (1978).

94. J. W. Lauber and R. Hoffmann, J. Am. Chem. Soc., 98, 1729 (1976) and references therein.

95. P. J. Johnson, S. A. Cohen, T. J. Marks, and J. M. Williams, J. Am. Chem. Soc., 100, 2709 (1978).

96. F. A. Cotton and T. J. Marks, J. Am. Chem. Soc., 91, 7281 (1969).

97. J. A. S. Smith and E. J. Wilkins, Chem. Commun., 381 (1965).

98. F. W. Faller and A. Davison, Inorg. Chem., 6, 182 (1967).

99. N. Serpone and K. A. Hersh, Inorg. Chem., 13, 2901 (1974).

100. R. C. Fay and A. F. Lindmark, J. Am. Chem. Soc., 97, 5928 (1975).

101. J. F. Harrod and K. Taylor, J. Chem. Soc., Chem. Commun., 696 (1971).

102. L. H. Pignolet, Top. Curr. Chem., 56, 91 (1975).

103. A. L. Arduini, J. Takats, and C. M. Lukehart, Abstracts of the 61st Canadian Chemical Conference, Winnipeg, Man., June 1978, IN 13.

104. a) D. G. Bickley and N. Serpone, Inorg. Chem., 15, 948 (1976).

b) D. G. Bickley and N. Serpone, Inorg. Chem., 15, 2577 (1976).

c) N. Serpone and D. G. Bickley, Prog. Inorg. Chem., 17, 391 (1972).

105. C. Oldham, Prog. Inorg. Chem., 10, 223 (1968).

106. J. Catterick and P. Thornton, Adv. Inorg. Chem. Radiochem., 20, 291 (1977).

107. A. Rosenheim and M. Kelmy, Z. Anorg. Allg. Chem., 206, 31 (1932).

108. K. W. Bagnall, MTP Int. Rev. Sci., Inorg. Chem., Ser. Two, 7, 41 (1975).

109. R. C. Paul, J. S. Ghotra, and M. S. Bains, J. Inorg. Nucl. Chem., 27, 265 (1965).

110. J. Selbin, M. Schober, and J. D. Ortego, J. Inorg. Nucl. Chem., 28, 1385 (1966).

111. K. W. Bagnall and O. M. Lopez, J. Chem. Soc., Dalton Trans., 1109 (1976).

112. M. Singh, R. Singh, R. Singh, and S. S. Sandhu, J. Indian Chem. Soc., 53, 1226 (1976).

113. I. Jelenić, D. Grdenić, and A. Bezjak, Acta Cryst., 17, 758 (1964).

114. P. C. Wailes and H. Weigold, J. Organomet. Chem., 24, 413 (1970).

115. R. B. King, Inorg. Chem., 5, 2231 (1966).

116. G. M. Larin, V. T. Kalinnikov, G. G. Aleksandrov, Yu. T. Struchkov, A. A. Pasnskii, and N. E. Kolobova, J. Organomet. Chem., 27, 53 (1971).

117. M. G. Harriss, M. L. H. Green, and W. E. Lindsell, J. Chem. Soc. A, 1453 (1969).

118. N. N. Vyshinskii, T. I. Ermolaeva, V. N. Latyaeva, A. N. Lineva and N. E. Lukhton, Dokl. Akad. Nauk. SSSR, 198, 1081 (1971).

119. R. B. King and R. N. Kapoor, J. Organomet. Chem., 15, 457 (1968).

120. A. A. Pasynskii, Yu. V. Skripkin, and V. T. Kalinnikov, J. Organomet. Chem., 150, 51 (1978).

121. M. R. Litzow and T. R. Spalding, "Mass Spectrometry of Inorganic and Organometallic Compounds", Elsevier, London, 1973, pp 559-573.

122. J. E. Drake, H. E. Henderson, and R. T. Hemmings, Inorg. Chem., 16, 1682 (1977) and references therein.

123. R. S. P. Coutts and P. C. Wailes, Aust. J. Chem., 20, 1579 (1967).

124. R. S. P. Coutts, R. L. Martin, and P. C. Wailes, Aust. J. Chem., 26, 941 (1973).

125. T. N. Tarkhova, E. A. Gladkikh, I. A. Grishin, A. N. Lineva, and V. V. Khalmanov, J. Struct. Chem. (Engl. Transl.), 17, 896 (1977).

126. S. D. Robinson and M. F. Uttley, J. Chem. Soc., Dalton, Trans., 1912 (1973).

127. C. Poder and J. R. Sams, J. Organomet. Chem., 19, 67 (1969).

128. K. Nakanishi and P. H. Solomon, "Infrared Absorption Spectroscopy", Holden-Day Inc., San Francisco, 1977.

129. R. A. Nyquist and W. J. Potts, Spectrochim. Acta, 15, 514 (1959).

130. V. V. Savant, J. Gopalakrishnan, and C. C. Patal, Inorg. Chem., 9, 748 (1970).

131. R. S. P. Coutts and P. C. Wailes, Aust. J. Chem., 21, 373 (1968).

132. J. Weidlein, J. Organomet. Chem., 32, 181 (1971).

133. J. Otera and R. Okawara, J. Organomet. Chem., 17, 353 (1969).

134. C. Santini-Scampucci and G. Wilkinson, J. Chem. Soc., Dalton Trans., 807 (1976).

135. J. Paris and G. Folcher, Can. J. Chem., 54, 1433 (1976).

136. L. Doretti, P. Zanella, G. Faraglia, and S. Faleschini, J. Organomet. Chem., 43, 339 (1972).

137. a) K. W. Bagnall, J. Edwards, J. G. H. duPreez, and R. F. Warren, J. Chem. Soc., Dalton Trans., 140 (1975).
b) K. W. Bagnall, J. Edwards, and F. Heatley, Proceedings, 4th International Transplutonium Element Symposium, W. Muller and R. Lindner, Ed., Elsevier, New York, N.Y., 1976, p 119.

138. V. K. Jain, B. S. Garg, and R. P. Singh, Aust. J. Chem., 30, 2545 (1977).

139. T. J. Pinnavaia and R. C. Fay, Inorg. Chem., 7, 502 (1968).

140. A. E. Comyns, Chem. Rev., 60, 115 (1960).

141. J. P. Fackler, Prog. Inorg. Chem., 7, 361 (1966).

142. U. Casellato, M. Vidali, and P. A. Vigato, Inorg. Chim. Acta, 18, 77 (1976).

143. H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, J. Am. Chem. Soc., 78, 2790 (1956).

144. E. W. Berg and J. J. Chiang Acosta, Anal. Chim. Acta, 40, 101 (1968).

145. H. A. Swain and D. G. Karraker, Inorg. Chem., 9, 1766 (1970).

146. G. Folcher, J. Paris, P. Plurien, P. Rigny, and E. Soulie, J. Chem. Soc., Chem. Commun., 3 (1974).

147. R. S. Marianelli, private communication.

148. K. W. Bagnall, private communication.

149. C. M. Lukehart and J. V. Zeile, J. Am. Chem. Soc., 99, 4368 (1977).

150. C. M. Lukehart and J. V. Zeile, J. Am. Chem. Soc., 98, 2365 (1976).

151. C. M. Lukehart and L. T. Warfield, Inorg. Chem., 17, 201 (1978).

152. C. M. Lukehart and G. P. Torrence, J. Chem. Soc., Chem. Commun., 183 (1978).

153. F. A. Cotton, Inorg. Chem., 3, 702 (1964).

154. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience Publishers, New York, N.Y., 1972, p 229.

155. M. M. Jones, B. J. Yow, and W. R. May, Inorg. Chem., 1, 166 (1962).

156. F. Calderazzo, M. Pasquali, P. Garibaldi, and T. Salvatori, Gazz. Chim. Ital., 104, 1145 (1975).

157. F. Calderazzo, M. Pasquali, and T. Salvatori, J. Chem. Soc., Dalton, Trans., 1102 (1974).

158. a) D. W. Thompson, Struct. Bonding (Berlin), 9, 27 (1971).

b) D. L. Kepert, Prog. Inorg. Chem., 23, 1 (1977).

159. R. C. Fay and R. N. Lowry, Inorg. Chem., 6, 1512 (1967).

160. R. W. Jones and R. C. Fay, Inorg. Chem., 12, 2599 (1973).

161. R. C. Fay and J. K. Howie, J. Am. Chem. Soc., 99, 8110 (1977).

162. V. W. Day, private communication.

163. C. S. Springer and R. E. Sievers, Inorg. Chem., 6, 352 (1967).

164. H. Kessler, Angew. Chem., Int. Ed. Engl., 9, 219 (1970).

165. G. Binsch in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, Chapter 3.

166. D. Kost, E. H. Carlson, and M. Raban, J. Chem. Soc., Chem. Commun., 656 (1971).

167. D. G. Bickley and N. Serpone, Inorg. Chim. Acta, 25, L139 (1977).

168. T. J. Marks and J. R. Kolb, J. Am. Chem. Soc., 97, 27 (1975).

169. K. P. Darst and C. M. Lukehart, private communication.

170. J. C. Green and O. Watts, J. Organomet. Chem., 153, C40 (1978).

171. H. O. Fröhlich and S. Kaiser, Z. Chem., 14, 486 (1974).

172. J. A. Hermann and J. F. Suttle, Inorg. Synth., 5, 143 (1957).